# Chemical cleaning of fouled membrane systems

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*Submitted for the degree of Ph.D.*

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# CHEMICAL CLEANING OF FOULED MEMBRANE SYSTEMS

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# PREFACE

The work described in this thesis was carried out in the Department of Chemical Engineering at the University of Bath, between October 1992 and October 1995. Financial support for this project came from the Engineering and Physical Sciences Research Council (EPSRC) under the Separations Initiative.

I wish to thank everyone who has helped and supported me throughout the project and in the writing of this thesis. In particular, my supervisors, Dr Michael Bird for giving me the opportunity to work on this challenging project, and Professor John Howell for his guidance, constant encouragement and humour. I would also like to extend my thanks to Mr Fernando Acosta for the technical support provided with the rig construction, Dr David Allen for his assistance with the HPLC work and Mr Colin Wilson for the photographic prints.

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On a personal note, my thanks goes to Gordana Spirovska and Elaine Odgers for their friendship and support. Last but not least, to my husband Christopher who will be very pleased when this is finally over!

29th June 1999

**Meloney Bartlett** **29/6/99**

# SUMMARY

Microfiltration techniques have found major applications within the food, biotechnology and water treatment industries. However, given the nature of the process fluids, membrane performance is habitually compromised by fouling. Therefore, the removal of deposited material is both a necessary and familiar step in maintaining the feasibility of the separation.

Chemical cleaning agents are generally used to restore membrane permeability and ensure hygienic process operation, but their application is typically empirical. Whilst these practical cleaning procedures are of industrial use, there has been little published information on the mechanisms involved. This thesis describes work which aims to increase the fundamental knowledge of membrane cleaning through a systematic study of the chemical, thermal and hydraulic parameters which affect the chemical cleaning process.

An experimental rig has been designed and constructed which produces fouled membrane samples and then cleans them *in-situ* under controlled thermo-hydraulic conditions. A systematic experimental study has evaluated the cleaning of flat-sheet, sintered stainless steel, ceramic and polymeric microfiltration membranes fouled with whey proteins deposits.

Flux recovery was used as the main criterion to assess membrane performance during cleaning procedures with water, sodium hydroxide, nitric acid and proprietary cleaning reagents. Concentration and temperature optima have been determined and the effects of crossflow velocity and transmembrane pressure described. Visual examination of the deposit by Scanning Electron Microscopy (SEM) and x-ray micro-analysis of the membrane surface before, during and after cleaning has been used to describe deposit removal, qualitatively. The use of HPLC to analyse retentate and permeate streams has facilitated cleaning mechanism descriptions.

The key mechanistic steps involved in flux recovery have been hypothesised. Qualitative and physical models have been developed which describe the experimental cleaning results.

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# NOMENCLATURE

| SYMBOL | DESCRIPTION | UNITS |
|---|---|---|
| **a** | Cross-section height | m |
| **A** | Area | $m^2$ |
| **A** | Pre-exponential factor | $Kgm^{-2}s^{-1}$ |
| **b** | Cross-section width | m |
| **BSA** | Bovine serum albumen | |
| $c_b$ | Solute concentration in the bulk | $kgm^{-3}$ |
| $c_m$ | Solute concentration at the membrane | $kgm^{-3}$ |
| $c_p$ | Solute concentration in the permeate | $kgm^{-3}$ |
| **C** | Concentration [Tzeng and Zall (1990)] | wt.% |
| **°C** | Degrees centigrade | |
| **CFV** | Crossflow velocity | $ms^{-1}$ |
| **d** | Pore diameter | m |
| $d_c$ | Capillary pore diameter | m |
| $d_{dep}$ | In-pore deposit thickness | m |
| $d_e$ | Equivalent pore diameter | m |
| $d_g$ | Particle diameter | m |
| $d_h$ | Hydraulic diameter | m |
| $d_o$ | Original pore diameter | m |
| **D** | Diffusion coefficient | $m^2s^{-1}$ |
| $E_A$ | Activation energy | $kJmol^{-1}$ |
| **EDTA** | Ethylene diamine tetracetic acid | |
| **°F** | Degrees Fahrenheit | |
| **F** | Conventional filtration | |
| **FR** | Flux recovery | |
| **FTIR** | Fourier Transform Infrared Spectroscopy | |
| **h** | Hour | 3600s |
| $h_k$ | Kozeny factor | |
| **HCl** | Hydrochloric acid | |

| | | |
|---|---|---|
| **$HNO_3$** | Nitric acid | |
| **HPLC** | High pressure liquid chromatography | |
| **g** | Gram | $1x10^{-3}$ kg |
| **IR** | Infrared | |
| **J** | Mass flux | $kgh^{-1}m^{-2}$ |
| **J*** | Steady state flux | $ms^{-1}$ |
| **$J_C$** | Cleaning flux | $kgh^{-1}m^{-2}$ |
| **$J_{FR}$** | Flux recovery | $kgh^{-1}m^{-2}$ |
| **$J_v$** | Velocity flux | $m^3s^{-1}$ |
| **$J_W$** | Water flux | $kgh^{-1}m^{-2}$ |
| **k** | Mass transfer coefficient | $ms^{-1}$ |
| **$k_\alpha$** | Removal rate constant | $s^{-1}$ |
| **$k_0$** | Zero order rate constant [Bird (1993)] | $ms^{-1}$ |
| **$k_1$** | First order rate constant [Bird (1993)] | $s^{-1}$ |
| **k** | First order rate constant | $s^{-1}$ |
| **$k_1$** | First order rate constant | $s^{-1}$ |
| **$k_{p1}$** | First order rate constant | $s^{-1}$ |
| **$k_{p2}$** | First order rate constant | $s^{-1}$ |
| **L** | Pore length | m |
| **l** | Litre | $10^{-3}m^3$ |
| **$l_c$** | Capillary pore length | m |
| **$l_g$** | Channel length through porous bed | m |
| **α-LA** | α-Lactalbumin | |
| **β-LG** | β-Lactoglobulin | |
| **ml** | Millilitre | $10^{-6}m^3$ |
| **μm** | Micron | m |
| **mm** | Millimetre | $10^{-6}$m |
| **mM** | Millimolar | $10^{-6}$ Moles |
| **MF** | Microfiltration | |
| **n** | Fouling index [Field et al (1995)] | |
| **N** | Number of pores | |
| **NaOH** | Sodium hydroxide | |

| | | |
|---|---|---|
| **nm** | Nanometre | $10^{-9}$m |
| **P** | Pressure [Tzeng and Zall (1990)] | lb.f.in$^2$ |
| **$\Delta$P** | Transmembrane pressure | bar ($10^5$Nm$^{-2}$) |
| **$P_i$** | Inlet pressure | bar ($10^5$Nm$^{-2}$) |
| **$P_o$** | Outlet Pressure | bar ($10^5$Nm$^{-2}$) |
| **$P_p$** | Permeate pressure | bar ($10^5$Nm$^{-2}$) |
| **PES** | Polyethersulphone | |
| **ppm** | Parts per million | |
| **PS** | Polysulphone | |
| **Q** | Volumetric flow rate | $m^3s^{-1}$ |
| **r** | Mass removal rate | kg $m^{-2}s^{-1}$ |
| **R** | Gas constant | kJ $mol^{-1}K^{-1}$ |
| **R** | Retention | |
| **$R_{ads}$** | Adsorption resistance | $m^{-1}$ |
| **$R_{cp}$** | Concentration polarisation resistance | $m^{-1}$ |
| **$R_C$** | Cleaning resistance [Daufin *et al* (1992)] | $m^{-1}$ |
| **$R_C$** | Cake resistance | $m^{-1}$ |
| **$R_F$** | Fouling resistance | $m^{-1}$ |
| **$R_I$** | In-pore blocking resistance | $m^{-1}$ |
| **$R_M$** | Membrane resistance | $m^{-1}$ |
| **$R_R$** | Removal resistance | $m^{-1}$ |
| **$R_S$** | Swelling resistance | $m^{-1}$ |
| **$R_{SOL}$** | Solute resistance | $m^{-1}$ |
| **$R_T$** | Total hydraulic resistance | $m^{-1}$ |
| **Re** | Reynolds number | |
| **RO** | Reverse osmosis | |
| **s** | Second | |
| **Sc** | Schmidt number | |
| **SEM** | Scanning Electron Microscopy | |
| **Sh** | Sherwood number | |
| **t** | Time | s |
| **T** | Absolute temperature | K |

| | | |
|---|---|---|
| **T** | Temperature [Tzeng and Zall (1990)] | °F |
| **TMP** | Transmembrane pressure | bar ($10^5 Nm^{-2}$) |
| **u** | Average linear velocity | $ms^{-1}$ |
| **UF** | Ultrafiltration | |
| **UV** | Ultraviolet | |
| **V** | Volume | $m^3$ |
| **WPC** | Whey protein concentrate | |
| **wt** | Weight | kg |
| **x** | Normal axial distance from membrane | m |
| **%** | Percentage | |

## GREEK

| | | |
|---|---|---|
| $\delta$ | Boundary layer thickness | m |
| $\delta$ | Model total deposit thickness[Bird (1993)] | m |
| $\delta x$ | Model unswollen deposit thickness [Bird (1993)] | m |
| $\delta y\chi$ | Model swollen deposit thickness [Bird (1993)] | m |
| $\varepsilon$ | Porosity | |
| $\eta$ | Kinematic viscosity | $m^2s^{-1}$ |
| $\mu$ | Dynamic viscosity | $kgm^{-1}s^{-1}$ |
| $\pi$ | Pi | 3.1427 |
| $\Delta\Pi$ | Osmotic pressure difference | bar ($10^5 Nm^{-2}$) |
| $\rho$ | Density | $kgm^{-3}$ |
| $\nu$ | Flow velocity | $ms^{-1}$ |
| $\chi$ | Swelling factor | |

# CHAPTER 1

# INTRODUCTION

## 1.0 THE NEED TO CLEAN

Microfiltration has become an industrial process of substantial technical and economic importance, having found major applications within the food, biotechnology and water treatment industries. Given the nature of the process fluids, membrane performance is habitually compromised by losses in permeability and selectivity due to membrane fouling.

Technical advances with membrane materials, as well as module and process design, have made it possible to delay the onset and reduce the amount of fouling in some cases (Section 2.2.4). Nevertheless, in practice, cleaning the membrane system is considered a necessary step in restoring performance and ensuring hygienic process operation.

## 1.1 DEFINITIONS AND CONCEPTS OF CLEANLINESS

The cleaning process involves the removal of extraneous materials from the system with the aim of restoring the surface to its pristine condition.

Cleaning is required to overcome the soil/membrane and soil/soil adhesion forces. The necessary energy required for deposit removal can be supplied by chemical cleaning agents, which react with the deposit and modify the interface, or kinetic energy provided in the form solution velocity and/or deposit shear stress. Thermal energy improves the reaction and hydraulic dynamics [Espig (1997)]. The energy to remove soil is usually supplied as a combination of all three. Compatible chemicals are used to remove the deposit in a crossflow system at elevated temperatures.

Generally, cleaning procedures applied to fouled membrane systems consist of a series of rinsing and cleaning cycles followed by a sanitation step. It is important to distinguish between the different procedures involved in the cleaning process.

When only water is used to remove deposited material the operation is called rinsing and any cleaning is by the mechanical action and solvating power of water. Nakanishi *et al* (1985), Plett (1985b) and Kulozik *et al* (1989) have extensively

reviewed the mechanisms of rinsing. The reader is directed to these studies for further information.

If a chemical agent is used the process is called cleaning or disinfection. Disinfection (or sanitation) is only concerned with the destruction of pathogenic micro-organisms and the reduction of organisms that degrade the product, where as cleaning entails the removal of all extraneous material [Luss (1984)]. Thus, it is implied that a clean surface should be free of any kind of soil. The degree of cleanliness required varies substantially from industry to industry. Romney (1990) summarised the three target levels of cleanliness as:

(i) **Physically clean** - free from visible impurities.

(ii) **Chemically clean** - free from chemical impurities.

(iii) **Biologically clean** - free from living micro-organisms.

The physical state of the membrane can be assessed by visual inspection. Physical action can be used to remove any gross deposits that are detected. It is not usually possible to remove strongly attached or adsorbed material, from the surface or pores of the membrane, by these physical means alone.

The removal of strongly attached material is possible through a combination of chemical and physical cleaning methods. Residual fouling or cleaning contamination affects the subsequent membrane performance, but is undetectable by visual examination. The adsorption of foulants and cleaning agents can cause irreversible changes to the membrane surface. This suggests that a used membrane can never be cleaned to its original pristine condition.

Reduction of the viable micro-organisms is possible through their removal or immobilisation. Cleaning processes are designed to remove micro-organisms and disinfection inactivates any that remain. The complex processes involved in the removal of micro-organisms and the disinfection of membrane surfaces have been considered by several researchers and the reader is directed to the work of Whitaker *et al* (1984), Luss (1985), Bigalke (1985), and Shorrock and Bird (1998) for further discussion of these problems.

The aim of the membrane cleaning process is to restore permeability and selectivity to the same level as found with a new membrane. However, the industrial reality is of a system where it is considered sufficient to clean the membrane such that its subsequent behaviour is standardised.

## 1.2 CLEANING PRACTICES

The need to develop practical cleaning methods, before significant scientific study could be initiated, has led to membrane cleaning procedures having been established on an empirical basis. In general, the cleaning and sanitation procedures applied to membrane systems in the food industry consist of a series of rinsing and cleaning cycles followed by a sanitation step, as shown in Table 1.1 [after Plett (1985)]

*Table 1.1 Basic steps in the cleaning procedure*

| Step | Function |
|---|---|
| **Pre-rinse** | Rinsing with water to remove gross, loose deposits |
| **Cleaning** | Removal of residual soil by a suitable detergent |
| **Inter-rinse** | Removal of any detergent and remaining deposit |
| **Sanitising** | Destruction of micro-organisms |
| **Post-rinse** | Removal of sanitisers from the system with water before resuming operation |

### 1.2.1 The Nature of Deposits

Deposits can be either simple product forms or fouling products in the form of a fouled layer. The type of deposit present will depend upon both the product, and the treatment applied to it (Section 2.2.3). From a cleaning point of view it is useful to classify typical deposits according to their nature and structure, as shown in Table 1.2

In practice, it is often necessary to apply different chemicals in series to obtain satisfactory cleaning when dealing with complex multicomponent food based deposits.

*Table 1.2* *Typical components in food deposits.*

| Component | Heat Induced Changes | Solubility | Removal |
|---|---|---|---|
| **Protein** | denaturatiion | water insoluble | difficult |
| | | alkali soluble | good |
| **Fat** | polymerisation | water insoluble | difficult |
| | | surfactant emulsification | good |
| **Sugar** | caramelisation | water soluble | easy |
| **Polysaccharides** | gelatinisation | water insoluble | difficult |
| **Mineral Salt** | precipitation | water insoluble | difficult |
| | | acid soluble | good |

### 1.2.2 The Study of Membrane Cleaning

Many earlier studies have concentrated on the cleaning of reverse osmosis (RO) and UF membranes fouled during water treatment [Belfort (1977)] and the aqueous effluents from the food, sewage, pulp and paper industries [Glemenius (1980), Buckley *et al* (1985), Winfield (1986) and Jacobs *et al* (1993)].

More recently the treatment of soluble oils has been considered by Lee *et al* (1984), as has the cleaning of membranes fouled with petrochemical wastes [Lahiere and Goodboy (1993) and Lindau and Jonsson (1994)].

The removal of removal soy flour extract from polysulphone UF membranes has been considered by Razavi *et al* (1996). Durham and Nguyen (1994) assessed the cleaning of hydrophobic membranes fouled during the osmotic distillation of tomato puree. The cleaning of ceramic microfiltration membranes fouled by apple juice [Padilla-Zakour and McLellan (1993)], or beer clarification [Wenten *et al* (1994), Gan and Howell (1994), Gan *et al* (1998)], have also been the subject of study.

The processing of dairy products remains the most significant application of pressure driven membrane processes in the food industry. Consequently, the majority of the literature deals with the removal of either milk or whey deposits by caustic or enzyme based cleaning agents.

Cleaning procedures for the removal of milk and whey protein deposits from process equipment are highly advanced and maybe adaptable to cleaning similar soils

from membrane surfaces. The mechanisms of removing whey protein deposits from stainless steel surfaces have been elucidated and models developed (Section 2.3.5). The transfer of this knowledge from hard surfaces to membrane systems is the novel concept central to this project.

### 1.2.3 Membrane Cleaning in the Dairy Industry

The two principle cleaning systems used reflect the nature of the deposit found during the processing of dairy products:

(i) **Two stage acid/alkali cleaners.** Typically hot sodium hydroxide (0.5 - 1.0 wt.%) is used to solubilise proteinaceous deposits, while a hot nitric acid wash (0.3 - 0.5% wt.%) is used to dissolve the inorganic salts or oxide films.

(ii) **Single stage commercial cleaning formulations.** There is widespread usage of proprietary cleaners formulated and marketed specifically for membranes, such as "Ultrasil" (Henkel Ecolab) and "DIVOS" (Diversey) [Leaver and Melling (1987)]. These cleaners are usually based on sodium hydroxide or an enzyme, with the addition of surfactants or sequestering agents.

Membrane manufacturers usually give guarantees, regarding minimum membrane lifetime for a defined application, only if the membranes are cleaned and disinfected according to instructions provided by them [Tragardh (1989)]. A survey by Leaver and Melling (1987) found that manufacturers relied heavily on experience and track record in offering their know how to users. Manufacturers also commonly develop and test their cleaning procedures on the users premises [Koch (1997)]. This has the advantage of using representative feed for evaluation of the cleaning regime.

## 1.3 ECONOMICS OF THE CLEANING PROCESS

Cleaning is expensive, as well as the cost of the chemicals themselves additional costs are incurred b due to:

- **Loss of production.** Up to 40% of the available production time may be used for cleaning [Wagner (1996)]

- **Product loss.** Contamination by ageing deposit or cleaning chemicals left by incomplete cleaning or insufficient rinsing makes the product unmarketable.

- **Labour costs.** Payment for an extra shift may occur if cleaning procedures cannot be incorporated within normal production.

- **Energy costs.** Required for the heating and pumping costs of large volumes of rinse water and cleaning solutions used.

- **Effluent treatment.** The use of strong or hazardous chemicals requires containment and treatment prior to discharge

Leaver and Melling (1987) reported that many users found that membrane lifetime were compromised by the cleaning procedures, thus, increasing the frequency of replacement. Capital costs are also increased, as system materials have to be compatible with the cleaning chemicals used.

It has long been considered that the economic and environmental impact of cleaning procedures would be reduced by decreasing the amount of cleaning chemicals used, and membrane lifetime extended by optimising the process conditions applied to MF systems.

## 1.4 SCOPE AND AIMS OF THE STUDY

The removal of deposited material is both a necessary and familiar step in maintaining the feasibility of MF separations. Despite the importance of cleaning there is little published information on the mechanisms involved. In the main, cleaning procedures have been established on a practical but empirical basis, concentrating on a final cleanliness criterion rather than determining the optimum cleaning conditions through the study of cleaning kinetics.

The aim of this work was to:

(i) develop an experimental system to investigate the effect of chemical agents on the cleaning of MF membranes fouled with proteinaceous deposits.

(ii) produce an extensive, systematic, study of cleaning in a fully defined system to determine the relative importance of key parameters - concentration, temperature, crossflow velocity and pressure.

(iii) elucidate the mechanisms of flux recovery and develop a model to describe the cleaning process.

These results could then be used to develop operational strategies for optimising membrane cleaning processes. The environmental impact of existing procedures could be reduced by decreasing the amount of chemicals used and by extending the lifetime of MF membrane systems.

## 1.5 THESIS ORGANISATION

Following this brief introduction this thesis is divided into six subsequent chapters.

Chapter 2 details the process and design considerations required for efficient membrane cleaning.

Chapter 3 describes the experimental system developed and classifies the materials and methods used.

Chapter 4 describes the results obtained through extensive experimental study and discusses them with reference to the relevant literature, while

Chapter 5 hypothesises the mechanisms of flux recovery and membrane cleaning models are developed to describe the experimental results.

Chapter 6 draws conclusions from the experimental and modelling work and makes recommendations and proposals for future work.

# CHAPTER 2

# PROCESS AND DESIGN CONSIDERATIONS

## 2.0 INTRODUCTION

The cleaning of MF membranes fouled during the processing of dairy fluids represents a significant and complex problem. In this chapter the literature is reviewed and the key process and design parameters which affect membrane cleaning are identified.

Research to date has shown that the nature of the membrane determines the efficiency of the process for a given application. Whilst the mechanical design and construction of the module affects cleanability the hygienic design of the auxiliary equipment is equally important.

Historically, work has concentrated on fouling and its reduction rather on cleaning. Understanding the nature of the fouling problem and how it affects the membrane's response to cleaning is a prerequisite to any cleaning study.

Selection of the appropriate cleaning agent and operating conditions affects not only deposit removal but also the time taken to restore membrane performance. The majority of cleaning work has focused on the final permeability of the membrane, which provides little information on the mechanisms of flux recovery. The production of kinetic data is required for the optimisation of cleaning procedures.

Modelling of the cleaning process is essential for the non-empirical design of cleaning systems. Existing models for the removal of proteinaceous deposits, from both hard and membrane surfaces are thus reviewed.

## 2.1 THE MEMBRANE PROCESS

Product separation is a fundamental operation in process industries. Membrane processes potentially offer separation solutions where materials are inherently difficult or expensive to separate. The mechanisms governing mass transport in different membrane processes vary as a function of the membrane type, equipment configuration and process conditions.

### 2.1.1 Microfiltration

Making use of a permiselective barrier to achieve separation, microfiltration (MF) relies on an applied hydrostatic pressure (< 2 bar) as the driving force to induce flow. The fundamental principle behind product separation is analogous to sieving, where MF works primarily by size exclusion, retaining larger particles or molecules but permitting smaller species to pass through the pores. MF membranes are available with nominal pore sizes varying from 0.05 μm to 10 μm making the process suitable for the separation of colloidal and particulate material (Figure 2.1).

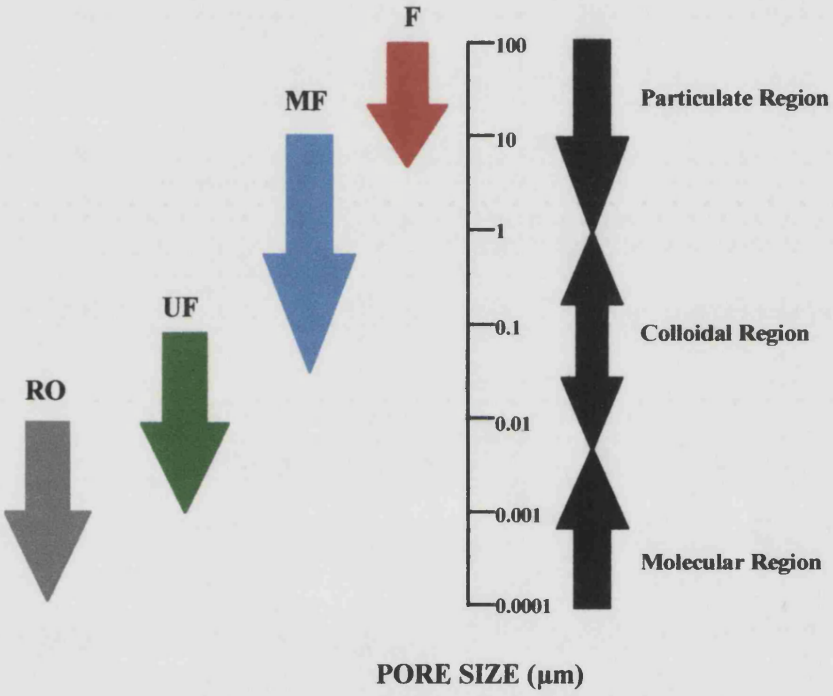



***Figure 2.1*** *Pore size ranges for conventional filtration (F), microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) processes*

#### *2.1.1.1 Membrane Development*

Fick produced the first synthetic MF membranes from nitro-cellulose in 1855. By the early 1900's German technologists had learnt to vary the pore size by varying polymer concentration but Sartorius-Werke was the first to start producing membranes commercially in 1927. However, these porous cellulose nitrate or cellulose acetate membranes were only used on a laboratory scale.

The early 1960's saw intensive research in the development of membranes for the removal of colloidal and macromolecular impurities from sewage effluent. The need for membranes with improved durability and better performance prompted the investigation of other materials. By the mid 1970's a large variety of thermally and chemically stable thermoplastics and polymers had been discovered which could be converted into a broad spectrum of MF membranes with high permeabilities. Today, MF membranes may be prepared from an extensive range of materials. These can be divided into organic (polymers) or inorganic (metals, ceramics, glasses) materials.

The choice of material for a certain application is not arbitrary but based on its specific properties. Factors such as the adsorption and wettability properties of the membrane can determine the performance. Inorganic membranes generally have better thermal and chemical resistance than organic membranes and are frequently used in harsh environments or for applications that necessitate frequent cleaning.

### *2.1.1.2 Microfiltration Applications*

In the last 30 years MF membranes have become industrial products of substantial technical and economic importance within the food, waste water and biotechnology industries, generating business in excess of 1 billion US dollars annually [Eykamp (1995)].

- **The Food And Beverage Industry**

  MF has found many applications within the dairy industry. Where it is used for the removal of bacteria from dairy fluids [Tragardh (1991)], the production of whey protein concentrates [Merin and Daufin (1990)], the fractionation of whey proteins [Mehra and Donnelly (1993)], the clarification of cheese brine, and the recovery of phosphocaseinate [Rosenberg (1995)] and others.

  Membrane filtration has rapidly replaced traditional treatments for the concentration and sterilisation of beverages. The technique is suitable for the filtration of fruit juices [Padilla-Zakour and McLellan (1993)], beer [Wenten *et al* (1994), Gan and Howell (1994)] and wine [Eykamp (1995)], because it does not affect the organophilic properties as severely as conventional treatments.

- **The water industry**

  MF systems for the processing of aqueous effluents from the food, pulp and paper industries are still under development [Glemenius (1980), Ridgeway (1983), Broom *et al* (1994), Yip *et al* (1996)]. The operation of MF, in conjunction with high-speed bioreactors, is an emerging technology for the treatment of municipal sewage, while the separation of oily wastewater's has been a standard industrial process since the 1970's.

- **The chemical and pharmaceutical industry**

  This is a major market for MF membranes which are widely used for the sterile filtration, concentration and purification of complex biological solutions such as antibiotics and blood products [Drioli (1986), Zhu *et al* (1993)].

- **Biomedical science**

  Medical applications include guarding against microbial and particulate contamination of fluids used in haemodialysis or for injection. MF plays an extensive role in maintaining the sterility of tissue cultures and other aseptic media applications. Furthermore, the potential of MF for virus removal continues to be developed [Satoh and Nakato (1995)].

In addition to these well-established applications there is a major effort to introduce MF into a wide variety of process applications. For successful and useful industrial operation the membrane must possess the following characteristics:

- Good performance - high permeability and selectivity
- High fouling resistance
- Mechanical durability, thermal stability and chemical resistance
- Long membrane life
- Easily cleaned and sterilised

### *2.1.1.3 Membrane Performance*

The performance or efficiency of a given membrane process is characterised by the permeation rate and/or retention characteristics of the membrane. To maintain performance frequent cleaning is required to remove surface and in-pore fouling which restricts flux and changes the selectivity of the process.

#### 2.1.1.3.1 Permeability

The permeation rate or flux ($J$) is usually considered to be the volume (l/hm$^2$) or mass flux (kg/hm$^2$) but can readily be converted to, $J_v$ the velocity flux (m$^3$s$^{-1}$).

Darcy's law shows that the capillary pores in MF membranes can be considered as cylindrical channels which traverse the membrane [Mulder (1991)]. Analogous to flow in a pipe, the flux through the membrane is directly proportional to the applied pressure ($\Delta P$). For a single pore with laminar flow, the volumetric flow ($Q$) is given as:

$$Q = \frac{\Delta P d^4 \pi}{128 \mu l} \qquad \textbf{(2.1)}$$

where $d$ is the pore diameter, $\mu$ is the viscosity and $l$ the pore length.

Thus, a membrane surface, of area $A$, with a number of pores, $N$, the membrane can be described by

$$J_v = Q\frac{N}{A} \qquad \textbf{(2.2)}$$

Thus, the Hagen-Poiseuille relationship is given as:

$$J_v = Q\frac{N}{A} = \frac{\varepsilon d_c^2}{32}\frac{\Delta P}{\mu l_c} \qquad \textbf{(2.3)}$$

where $\varepsilon$ is the porosity of the membrane.

However a large number of pore geometries exist and modifications have been made to account for non-cylindrical and tortuous pores. Flow through a nodular membrane has been equated to flow through a packed bed [Carmen (1937)].

$$J_v = \frac{\varepsilon^3 d_g^2}{36 h_k (1-\varepsilon)^2} \frac{\Delta P}{\mu l_g} \qquad (2.4)$$

In both Equations (2.3) and (2.4) the flux is inversely proportional to viscosity ($\mu$) and the equations relate volume flow to simple structural parameters such as porosity ($\varepsilon$) and pore diameter ($d$). The flux is proportional to the porosity in membranes with capillary pores where as in tortuous types of structure the dependence on porosity is more complex. Figure 2.2 illustrates the relationship between the pore diameter, $d_c$, in a membrane with capillary pores and the diameter of a particle, $d_g$, in a nodular type of membrane structure.

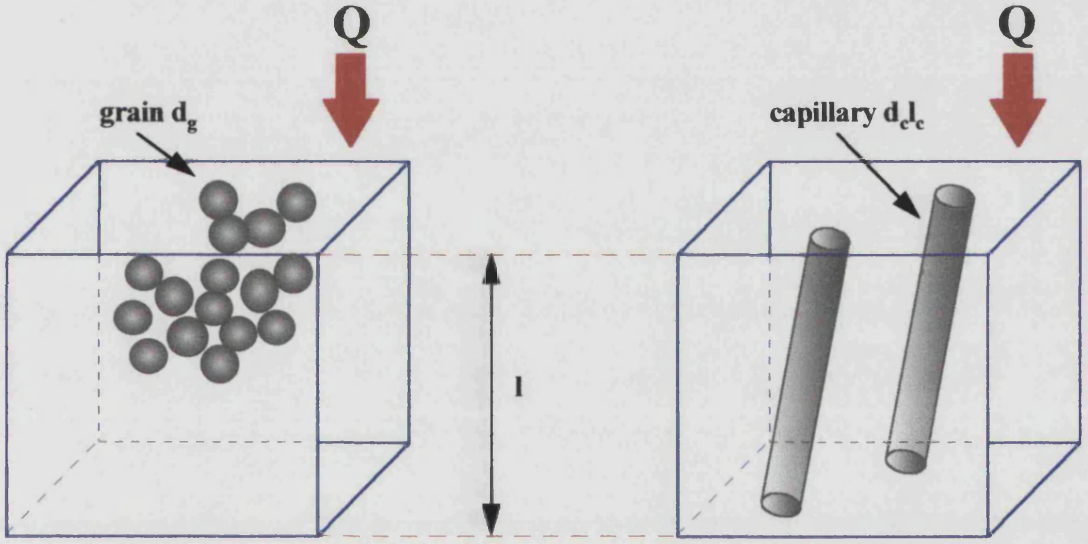



***Figure 2.2*** *Comparison of flow through a packed bed and through capillary pores*

A proportional relationship between $d_c$ and $d_g$ is given by comparing Equations (2.3) and (2.4)

$$\frac{d_g^2}{l_g} \propto \frac{d_c^2}{l_c} \qquad (2.5)$$

The permeation rate in inversely proportional to the thickness of the actual barrier layer ($l$). MF membranes can be up to 150 μm thick and if a porous symmetrical structure is used the complete membrane thickness contributes to transport resistance. An asymmetric or composite membrane, which consists of a relatively thin active layer supported by a porous substructure, has a much higher permeability than a membrane with comparable total thickness,. For high water permeability it is essential to ensure that the structural parameters are such that the active layer thickness is as thin as possible, the porosity is as high as possible and the pore size distribution is as narrow as possible.

#### 2.1.1.3.2 Selectivity

For dilute mixtures consisting of a solvent (usually water) and a solute the selectivity is usually expressed in terms of retention, $R$, towards the solute. The solute is partly or completely retained while the solvent passes freely through the membrane. $R$ is given by:

$$R = \frac{c_b - c_p}{c_b} = 1 - \frac{c_p}{c_b} \qquad \textbf{(2.6)}$$

where $c_b$ is the solute concentration in the feed and $c_p$ is the solute concentration in the permeate. $R$ is dimensionless and does not depend upon the units in which the concentration is expressed. The values of $R$ vary between 1 (complete retention of solute) and 0 (solute and solvent pass through the membrane freely).

Membrane rejection is complex and dependent not only on the molecular size and shape but the mutual exclusion between solute molecules as well as the operating conditions of the process.

### *2.1.1.4 Membrane Resistance to Fouling*

That pore characteristics govern the filtration behaviour of MF membranes is rather simplistic. The nature of the material constituting the membrane matrix contributes to the possibility of interaction between the filter and the medium. Membrane function is influenced, and often deteriorated, by the effects of filtrate contact. Careful choice of

the membrane material is essential to maximise compatibility for optimum separation and reduce the frequency of fouling.

By studying adsorption, coating materials and surface modifying functional groups can be preselected to reduce the interaction forces between the filtrate and the membrane. Recent work by Nystrom and Zhu (1996) has shown that hydrophilic polysulphone based UF membranes resisted internal fouling by proteins and were therefore easier to clean than hydrophobic membranes examined in the study. Generally, hydrophobic materials have been found to have a greater tendency for fouling. Preadsorption of synthetic hydrophilic polymers on to hydrophobic MF and UF membranes can reduce the susceptibility of the modified membranes to protein fouling. Bauser *et al* (1982) coated Cuprophan® HDF and Nuclepore® membranes with carbon, titanium and polysiloxane films to successfully reduce the adsorption of proteins to the membrane surface. Le and Howell (1983) found precoating UF membranes with polyethylene glycol resulted in a less severe flux decline and greatly facilitated membrane cleaning. By modifying UF membranes with hydrophilic biopolymers Brink *et al* (1993) also found it was possible to reduce adsorption by steric repulsion. Fouling was reduced due to partial sealing of the pore entrance and prevention of internal protein adsorption. Nevertheless, the blockage of the larger MF pores could not be averted by these preadsorption techniques. Chen *et al* (1992) showed that the preadsorption of small molecules such as anionic surfactants, to coat the membrane surface, might reduce the observed water flux. However, Fane (1995) demonstrated that this 'masking' of pores may have a positive effect on the product flux by reducing the amount of in-pore fouling.

In general membranes which retain the fouling layer upon the surface are easier to clean than membranes which allow fouling material to enter the porous structure [Leaver and Melling (1987)].

#### *2.1.1.5 Membrane Durability*

The chemical, thermal and physical resistance of membranes can be limiting factors not only for the filtration process but also for the cleaning process.

The use of excessive pressures and temperatures during operation may cause polymeric membranes to undergo irreversible compaction, membrane 'creepage' or the

separation of the membrane from its supportive backing material. These phenomena can permanently alter the permeability and selectivity of the membrane [Cheryan (1986)].

In general, the cleaning methods employed are often dependent upon the construction of the membrane itself. Backflushing techniques can only be applied to hollow-fibre and rigid microporous membrane systems, which are capable of withstanding the pressures applied to induce reverse flow.

The choice of cleaning agent and process temperature are often limited by the material used for the membrane and the fabrication of the membrane module [Smith and Bradley (1986), Smith (1990), Bohner and Bradley (1992)]. The use of cellulose acetate membranes precludes the use of hot alkali, as these membranes can only be used in the pH range 3-8 and up to 40°C. However, the development of non-cellulose membranes has lead to an increase in membrane resilience. Polymeric membranes, made of materials such as polysulphone, are resistant to pH 1-13 using temperatures up to 80°C. Inorganic membranes, composed of metals, metal oxides or carbon based materials, are generally considered to have good chemical and thermal resistance, being able to withstand severe chemical cleaning regimes and high temperatures [Tragardh (1989), Daufin *et al* (1991-1993), Wenten *et al* (1994), Gan *et al* (1998)].

#### *2.1.1.6 Membrane Lifetime*

The operational life of a membrane is not indefinite. The membrane life ends when membrane performance no longer meets specific performance criteria. Membranes deteriorate during processing and cleaning, however it is difficult to separate the effect each has on membrane life.

It is known that the use of excessively severe cleaning chemicals and procedures reduces not only membrane lifetime but also that of auxiliary equipment [Smith (1990)]. Membrane users have found that each caustic cleaning procedure can reduce the lifetime of cellulose acetate membranes a 1000 times faster than each filtration run [Leaver and Melling (1987)]. Wagner (1996) found that non-ionic surfactants caused stress corrosion of polysulphone membranes.

The presence of contamination in process feeds which irreversibly foul or damages membranes can limit the membrane lifetime. Luss (1985) found that

defoamers, directly adsorbed by the membrane, caused a severe and permanent flux decline. Field experience indicated that membranes operating in what was a supposedly similar environment might have widely differing lifetimes [Armishaw (1982), Luss (1985)].

With the development of more durable materials and a greater understanding of the up-stream process parameters which limit membrane lifetime the economical feasibility of MF processes is enhanced compared to conventional technologies.

### 2.1.2 Module Design

For membrane equipment on both laboratory and industrial scale, membranes are supplied in the form of modules. In general modules are designed to provide adequate support for the membrane and provide a large membrane area to volume ratio. The module design should not promote fouling and should be easily cleaned and sanitised.

A number of module designs are available (Table 2.1). Capillary and hollow-fibre modules are based on the tubular membrane configuration. Plate and frame, as well as spiral wound modules, are based on flat sheet membranes with spacers in the feed and/or permeate channels. The choice of module is determined by the application and the economics of the configuration.

*Table 2.1 Comparison of standard membrane modules*

| | **Plate & Frame** | **Spiral Wound** | **Tubular** | **Hollowfibre** | **Capillary** |
|---|---|---|---|---|---|
| **Packing Density** | moderate | high | low | moderate | very high |
| **Plant Investment** | high | low | high | very high | moderate |
| **Operating Costs** | moderate | low | high | moderate | low |
| **Membrane Only Replacement** | yes | no | yes/no | no | no |
| **Fouling Tendency** | moderate | moderate | moderate | low | very high |
| **Cleanability** | good | low | good | low | none |

Several design factors influence the cleanability of membrane configurations, as shown in Table 2.2. The prevention of dead spots on both sides of the membrane is essential. In addition, the permeate compartment should have as little hold-up as possible and should be filled with liquid throughout. If the volume is large it would make it difficult to wash out the permeate hold-up without using and large volumes of water or cleaning agents [Le and Howell (1985)]. Module design should ensure that the cleaning, sanitising or flushing solutions reach all parts of the system.

*Table 2.2* *Summary of cleanability for membrane configurations*

| Configuration | Channels (mm) | Access to Permeate Side | Access to Retentate Side | Cleanability |
|---|---|---|---|---|
| **Plate & Frame** | 0.2-1.0 | Good | Good | Good |
| **Spiral Wound** | 1-3 | None | None | Moderate |
| **Tubular** | 6-25 | Good if unshrouded<br>Poor if shrouded | Moderate | Good |

If good sanitary design practice is not followed ageing process material and micro-organisms will collect in dead ends and crevices and affect the product quality [Cheryan (1986)]. The principles of good hygienic design should not only apply to the membrane module, but also the components of the auxiliary system including pressure gauges, manifolds and pumps. Considering process hygiene from the start of a project will allow many potential problems to be eliminated at the design stage. As the project progresses it becomes more difficult and, therefore, more expensive to put things right.

### 2.1.3 Process Design

Conventional filtration processes operate in dead-end mode, where the flow is normal to the face of the filter, and the feed is forced through the membrane. This implies that the concentration of rejected components in the feed increases and consequently the quality of the permeate decreases with time [Mulder (1991)].

Conventionally, UF is carried out crossflow mode, with the principle flow parallel to the surface of the membrane. A simple crossflow system concentrates the

process feed by pumping it from a holding tank and across the membrane at the appropriate velocity, 1.0 - 8.0 $ms^{-1}$ [Coulson and Richardson (1991)]. The solvent permeates through the membrane and the feed emerges in a more concentrated form. The partially concentrated retentate is recycled to the tank for further processing, while the permeate is stored or discarded as required.

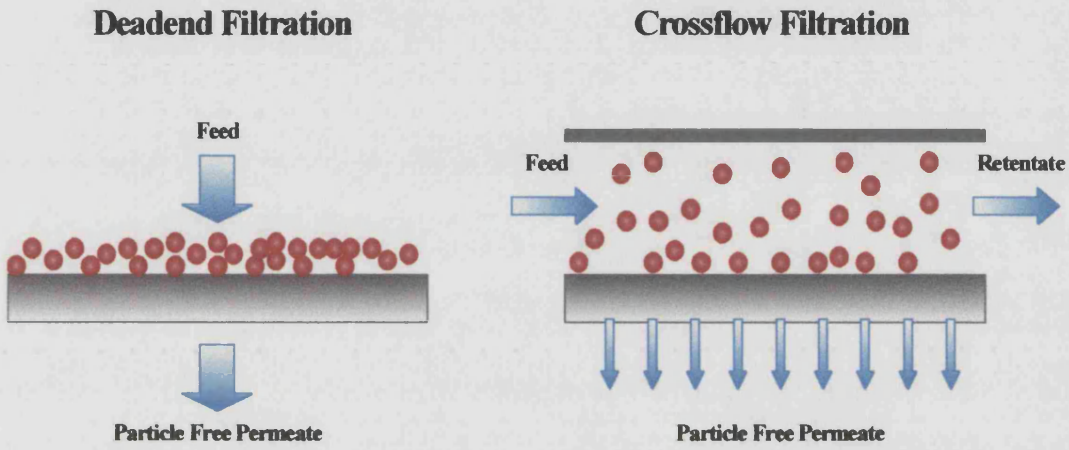



***Figure 2.3*** *Schematic representation of dead-end and crossflow filtration*

MF is practised both ways (Figure 2.3). For industrial applications, crossflow operation is preferred because of the lower fouling tendency relative to dead-end operation. The washing action of the fluid passing tangential to the surface of the membrane, ideally, keeps the filter from becoming clogged. Perfectly, crossflow operation would be a process without the deposition of material. The flux decrease occurring during crossflow MF shows that this is not the case. In practice the permeation rate falls with time due to concentration polarisation and membrane fouling phenomena.

## 2.2 THE FOULING PROCESS

Given the complex nature of the process fluids, MF performance is habitually compromised by a progressive flux decline that has a negative influence on the economics of a process. The mechanisms of flux decline and methods used to reduce these process limitations are discussed in this section.

### 2.2.1 Characteristic Flux Behaviour

Considering a solution where the solvent is freely transferable, the convective flow through the membrane can be described by Equation 2.7.

$$J_v = \frac{\Delta P - \Delta\Pi}{\mu(R_M + R_S)} \qquad (2.7)$$

Where $\Delta P$ is the hydrostatic or transmembrane pressure, $\Delta\Pi$ is the osmotic pressure, $R_M$. is the hydraulic resistance of the membrane and $R_s$ is the additional resistances arising from the presence of solute.

The osmotic pressure of most solutes encountered in MF can be considered as negligible [Mulder (1991)], hence, the pure water flux is expressed as:

$$J_v = \frac{\Delta P}{\mu R_M} \qquad (2.8)$$

$R_M$ may be determined experimentally at fixed pressure, temperature and crossflow velocity. Assuming that the physical properties of the membrane remain unchanged throughout the membrane lifetime, then $R_M$ is a constant and independent of other parameters. Membrane behaviour is typically defined by its pure water flux.

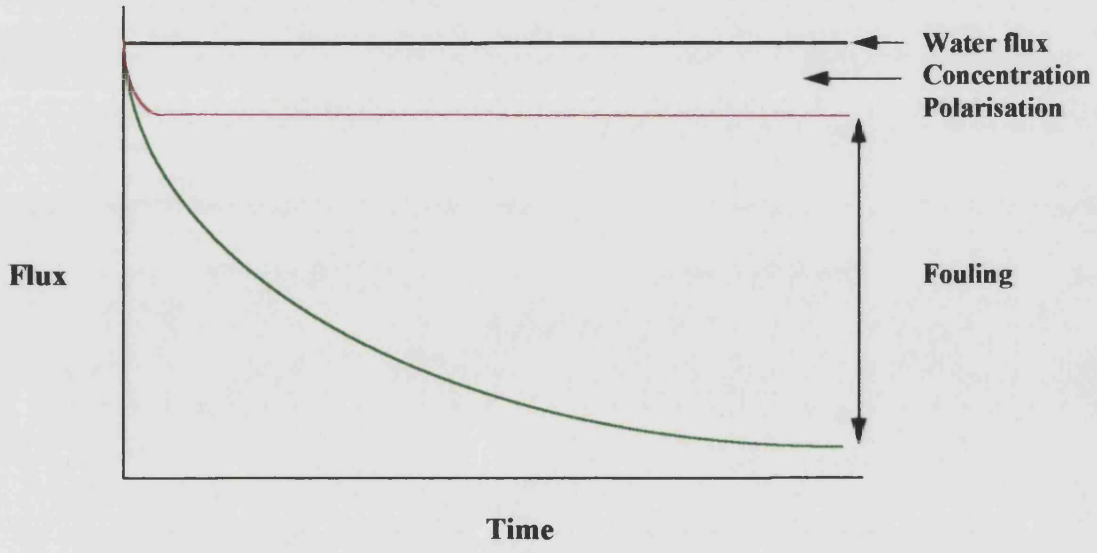



***Figure 2.4*** *Typical flux profile for the separation of macrosolutes during MF*

Generally, during the separation of macromolecular solutions a decline in permeation rate with time is observed (Figure 2.4). For MF the flux decline can be very severe, with the process flux often being less than 5% of the pure water flux [Mulder (1991)]. This flux decline can be caused by several factors that induce additional feed side resistance to transport across the membrane.

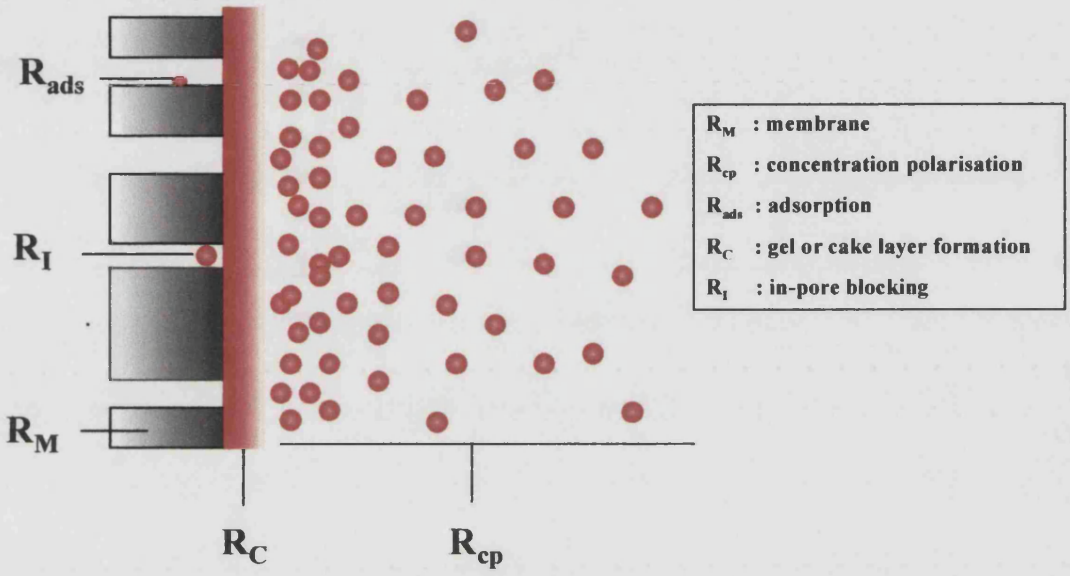



***Figure 2.5*** *Overview of the types of resistance towards mass transfer in MF [Mulder (1991)].*

During MF solutes adsorb to the membrane surface $R_{ads}$ (Figure 2.5) and molecules build up at the membrane surface causing a resistance to permeation due to concentration polarisation, $R_{cp}$. The concentration of the accumulated layer may become so high that a gel or cake layer can be formed, exerting a resistance, $R_C$. With porous membranes it is possible for solute to penetrate the membrane and block the pores, giving a resistance to flow, $R_I$. Such that

$$R_{SOL} = R_{cp} + R_{ads} + R_C + R_I \qquad \textbf{(2.9)}$$

The resistance due to the membrane itself and the sum of all other resistances arising from the presence of the solute, $R_{SOL}$ can be described as the total hydraulic resistance in series $R_T$.

$$R_T = R_M + R_{SOL} \tag{2.10}$$

Consequently

$$J_v = \frac{\Delta P}{\mu R_T} \tag{2.11}$$

### 2.2.2 Concentration Polarisation

Solution flowing tangential to the membrane surface is forced to the membrane interface by an applied hydrostatic pressure. Separation of solute and solvent takes place when the solvent passes through the membrane and solute, transported to the membrane surface by convective forces, is retained. This increase in the local concentration, at the membrane surface, is termed concentration polarisation.

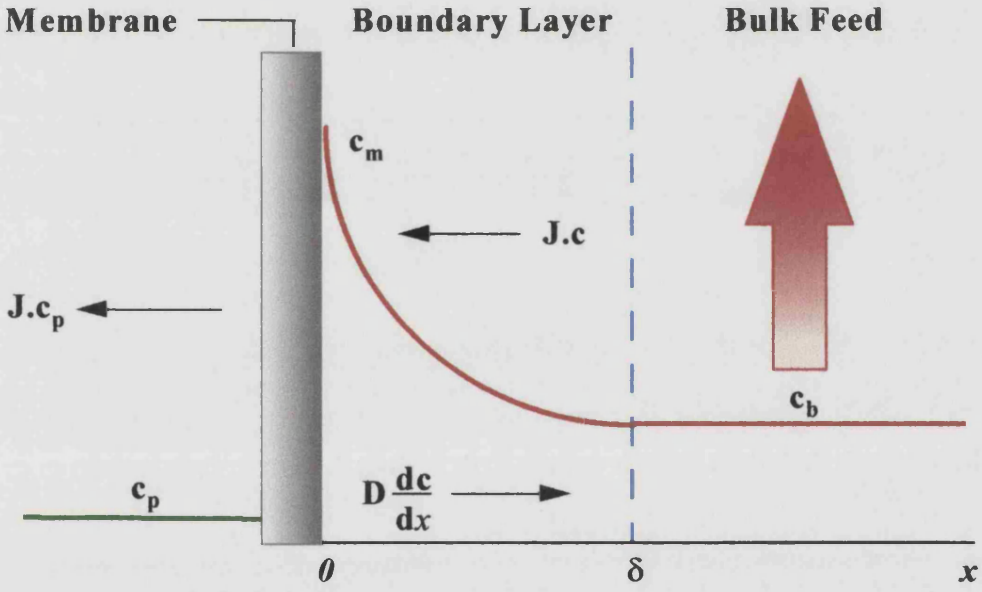



***Figure 2.6*** *Concentration polarisation: concentration profile under steady state conditions*

A fraction of the rejected solute will diffuse back into the bulk flow where the concentration is lower and a concentration gradient is established, as illustrated in Figure 2.6. At steady state the convective flow to the membrane will equal the sum of solute leakage and the rate of back diffusion.

$$J.c = D\frac{dc}{dx} + J.c_p \qquad (2.12)$$

Where the boundary conditions are

$$x = 0 \rightarrow c = c_m$$
$$x = \delta \rightarrow c = c_b$$

Integrating Equation 2.12 results in

$$J.c = \frac{D}{\delta}\ln\left[\frac{\left(c_m - c_p\right)}{\left(c_b - c_p\right)}\right] \qquad (2.13)$$

Where the ratio of the diffusion coefficient, $D$, and the thickness of the boundary layer, $\delta$, is called the mass transfer coefficient.

$$k = \frac{D}{\delta} \qquad (2.14)$$

Generally, for MF processes with high permeation rates, convective transport of solutes is high and the diffusion coefficients relatively small [Eykamp (1995)]. Thus, the consequences of concentration polarisation can be very severe, exerting a considerable resistance to mass transfer [Le and Howell (1985)]. However, concentration polarisation is a reversible process. When the applied hydrostatic pressure is released the shearing effect of the crossflow will generally remove all the solute particles away from the membrane surface, restoring flux.

### 2.2.3 Membrane Fouling

Fouling is a blanket term used to cover the physiochemical causes of flux decline and loss of selectivity that are not reversed when transmembrane pressure is relaxed [Cheryan (1986)]. It is generally considered that fouling occurs in two stages.

The first, causes the adsorption of solutes to the membrane by hydrogen bonding, van der Waals forces, entropic or electrochemical interactions [Aimar (1993)]. This can occur rapidly, and may be observed by wetting a membrane with a process fluid, without applying pressure [Gan (1992)]. Adsorption has a major impact on membrane performance, causing as much as a ten-fold reduction in the hydraulic permeability of the membrane compared to the initial water permeation rate [Le and Howell (1985)]. In addition, the observed retention can be increased particularly in mixtures of macromolecular solutes [Heinemann *et al* (1988)].

The second stage is characterised by a slow degradation of the membrane flux due to the deposition of material from the bulk solution [Eykamp (1995)]. Deposition causes partial or complete blocking of the membrane pores and a progressive cake build-up on the membrane surface.

### *2.2.3.1 Deposit Formation*

The severity of membrane fouling will depend upon both the feed and the treatment applied to it. The parameters that affect deposition may be considered as:

- **Physiochemical** - the composition of the feed, presence of salts, pH and heat treatment.
- **Process** - feed concentration, temperature, flowrate and pressure.

Depending on the type of feed and the environmental conditions of the process a number of mechanisms can occur which lead to the formation of a deposit.

(i) **Particulate fouling** - the accumulation of particulate material originally suspended in the feed.

(ii) **Chemical precipitation** - as feed stream becomes concentrated the solubility of some components may be exceeded resulting in their precipitation. Increasing temperature can cause some salts to prcipitate out, due to inverse solubility. For salts where the solubility decreases with decreasing temperature deposition can occur when the process fluid is cooled.

(iii) **Reaction fouling** - foulants are formed by chemical reaction either in the bulk fluid or on the membrane surface.

(iv) **Colloidal fouling** - material may be deposited due to colloidal charge or size characteristics.

(v) **Biological fouling** - Micro-organisms attached to the membrane.

Due to the complex nature of fluids, such as milk and whey, deposit formation can be caused by multiple mechanisms.

### *2.2.3.2 Dairy Fouling*

Milk is an aqueous solution of proteins, lactose, minerals and vitamins that carries emulsified fat globules and colloidal dispersed casein micelles consisting of proteins, phosphates, nitrates and calcium. If the fat is removed from the milk the product is called skim milk. If the casein is precipitated out the residue is known as whey [Coultate (1992)].

*Table 2.3 Typical protein composition for WPC, whole and skim milk.*

| | Whole Milk g/l | Skim Milk % | W P C % |
|---|---|---|---|
| **Casein Proteins** | **27** | **80** | **0** |
| α-casein | 14 | 40 | |
| β-casein | 8 | 24 | |
| κ-casein | 4 | 12 | |
| γ-casein | 1 | 4 | |
| **Serum Proteins** | **7** | **20** | **100** |
| β-lactoglobulin | 1 - 8 | 5 | 50 |
| α-lactalbumin | 2 - 4 | 12 | 15 |
| immunoglobulins | 0 - 7 | 2 | 8 |
| others | 0 - 3 | 1 | 27 |

Ultrafiltration and spray drying of the whey produces whey protein concentrate (WPC) powder, with serum protein concentrations varying from 35% to 95%. The typical protein composition of whole and skim milk, as well as a typical 35% WPC powder [Carbelac 35, supplied by Carbury Milk Products Ltd], is given in Table 2.3.

Four major components contribute to the fouling of membrane systems by dairy fluids - proteins, minerals, lipids, lactose. It is primarily the physiochemical properties of these components and interactions between them that causes changes to the deposit formation and the subsequent permeate flux.

Proteins are considered the major source of membrane fouling during dairy fluid processing. Proteins are a class of substances particularly susceptible to adsorptive forces as these compounds do not have a fixed conformation.

Daufin *et al* (1989) found that complex interaction between the membrane surface and protein represented the basic step of fouling during ultrafiltration of defatted whey, which was confirmed by the work of Labbé *et al* (1990). Lee and Merson (1975) showed that the rapid formation of surface deposit with cottage cheese whey was rapid. SEMs of milk fouled, ceramic, MF membranes showed that the deposition was initiated by adsorption of a thin layer film of casein salts on which were deposited other micelles [Vetier *et al* (1988)]. Attia *et al* (1991) and Kim *et al* (1992) showed that deposition was linked to the physiochemical state of the milk, where individual micelles formed at pH 6 - 6.2 while chains and clusters predominated between pH 5 - 6.

Lee and Merson (1975) showed that fouling with cottage cheese whey was a series of events initiated by relatively large particles. Protein complexes formed a porous matrix on the membrane surface followed by finer grain materials, such as β-lactoglobulin (β-LG) and bovine serum albumin (BSA), which filled in the matrix and formed sheets over the membrane. α-Lactalbumin (α-LA) formed smooth round spherical particles which did not hinder water permeation greatly. Daufin *et al* (1993) was in agreement with these findings. Their results showed that the main foulants responsible for the heterogeneous fouling of ceramic UF membranes during defatted whey processing were calcium aggregates and proteins. Nevertheless, Cheryan (1986) could show no difference in the manner in which individual whey proteins deposited. Vetier *et al* (1988) proposed that the proportion of casein to serum proteins in whole

milk deposits was the same. However, Tzeng and Zall (1990)] proposed that the deposition of casein and serum proteins was dissimilar in the ultrafiltration of skim and whole milk. But both concluded that proteins formed a disproportionate percentage of the deposit.

Lee and Merson (1975) and Daufin *et al* (1993) showed that calcium phosphates play major roles in membrane fouling for cheese whey systems. As well as forming aggregates or protein-mineral complexes that interact with the membrane, salts can precipitate out of solution causing a flux reduction. Salts can also contribute to the ionic strength of the solution, which in turn affects the conformation, and dispersion of the proteins [Heinemann *et al* (1989)].

SEM examination of milk fouled, ceramic, MF membranes by Vetier *et al* (1988) showed that fat globules gave the deposit special structural qualities - different porosity, permeability and resistance to mass transfer. In the presence of soluble oils, lipids and fats the membrane's performance generally deteriorates with time. Evidence indicates that the removal of these substances has a beneficial effect on membrane flux [Lee and Merson (1975)].

Even though lactose has limited solubility this low molecular weight compound does not have a significant role in fouling. Whilst the viscosity of lactose solution is higher than that of pure water it is not considered a problem for the processing of milk and whey because of the degree of concentration typically possible with membranes [Smith (1990)]

Figure 2.7 shows how processing factors such as pH, concentration and temperature affect fouling for certain key components. Proteins are least soluble near their isoelectric point. Therefore, concentration polarisation and subsequently fouling increases because the proteins are more likely to aggregate. β-LG has an isoelectric point at pH of 5.2, α-LA has an isoelectric point at pH 4.8 and BSA has an isoelectric point at pH 5.1 [Nilsson (1988)]. Daufin *et al* (1993) observed that the transmission of β-LG during the filtration of dialysed whey dropped from about 95% at pH 8 to 60% at pH 5. The pH of whey and milk solutions affects not only the protein but the mineral solubility as well. As the pH increases calcium becomes less soluble, and therefore, calcium phosphate complexes are more likely to precipitate on to the membrane or within pores resulting in decreased flux.

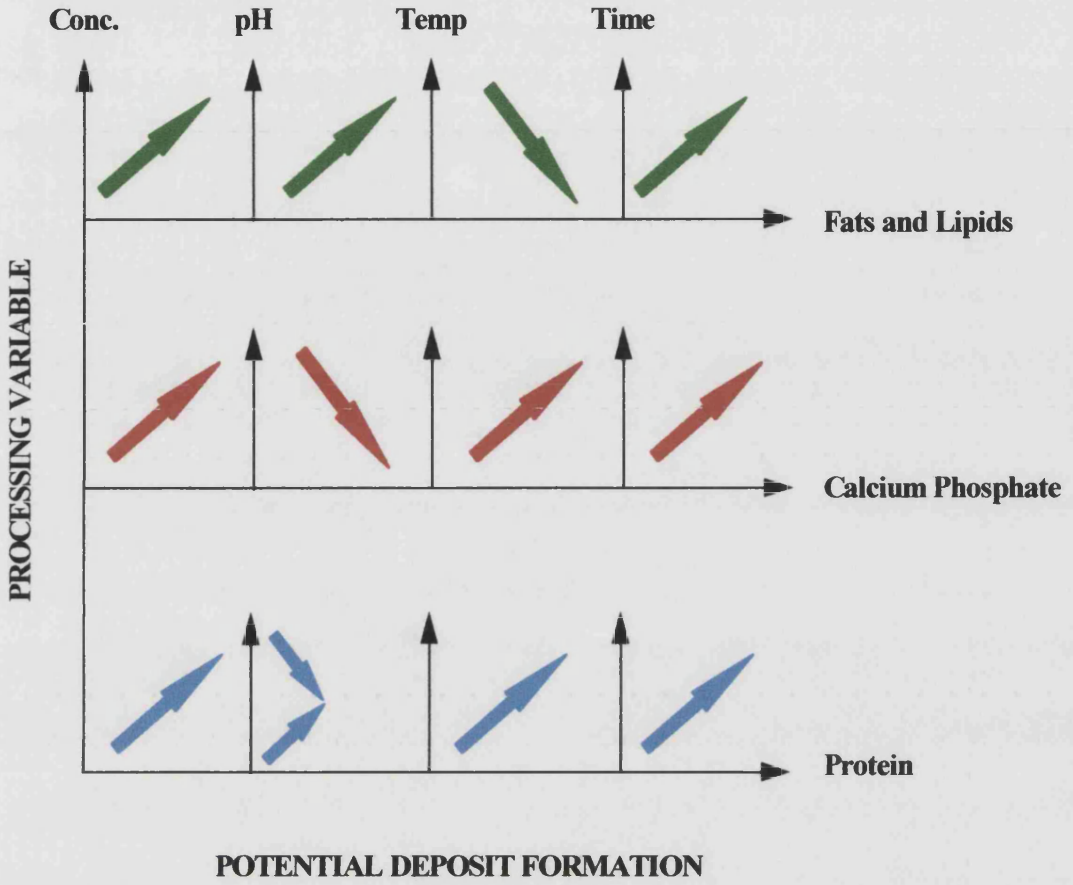



***Figure 2.7*** *Potential deposit formation due to interaction between the processing variable and the fouling component [after Luss (1984)]*

The formation of deposit on membrane surfaces by milk and whey proteins is highly dependent on the temperature of the process as well the pH [Wahlgren and Arnebrant (1989)]. Low temperature processing has the advantage of minimising mineral deposition and microbial growth, although this is done at some expense to flux [Luss (1985)]. The general opinion is that as the temperature increases, resulting in higher flux rates, that the beneficial effects such as lower viscosity and higher diffusivity will outweigh the detrimental effects of low salt solubility.

Feed velocity or shear stress at the membrane surface influences fouling and the accompanied flux decline. Severe fouling can often be the effect of low velocities. The crossflow velocity should have a minimum value of 1.0 $ms^{-1}$ for MF systems [Coulson and Richardson (1991)]. High shear stress rates generated at the membrane surface should tend to shear off deposited material [Belfort (1989)]. However,

velocities that are too high do not provide enough retention time for mass transfer and will sweep away the dynamic layer [Lahiere and Goodboy (1993)].

Flux, *J*, is considered to be proportional to the applied pressure, but as pressure is increased the polarisation layer reaches a limiting concentration where flux becomes independent of pressure and becomes mass transfer controlled. High transmembrane pressures may restrict the back diffusion of material from the fouling layer further aggravating the fouling problem. Higher pressures can increase fouling and cause compaction of the fouling layer. Consequently, Cheryan (1986) found increasing pressure above a critical point resulted in a lower flux for acid whey ultrafiltration in a spiral wound module.

Using high initial solid levels severely compromises flux as the fouling layers severely reduce both the permeability and selectivity of the membrane. Taddei *et al* (1988) showed that protein rejection was not generally affected if, instead, whey was allowed to concentrate to high protein levels over a period of time. However, they found that the irreversible fouling resistance for concentrated whey solutions was about double after rinsing the deposit.

### *2.2.3.3 Fouling Mechanisms*

The deposition of material from complex, multicomponent fluids, such as dairy products, has been considered to follow several different patterns. Bowen *et al* (1995) explained the fouling of MF membranes in terms of the successive or simultaneous presence of the following stages:

**(i)** the smallest pores are blocked by particles arriving at the membrane surface

**(ii)** the inner surface of the bigger pores are covered

**(iii)** some particles arriving at the membrane cover particles already deposited while others directly block some of the pores.

**(iv)** finally a cake build up occurs

### *2.2.3.4 Dynamic Fouling Models*

During the past 25 years numerous theoretical attempts have been made in an effort to understand permeate decline due to blocking in microfiltration systems.

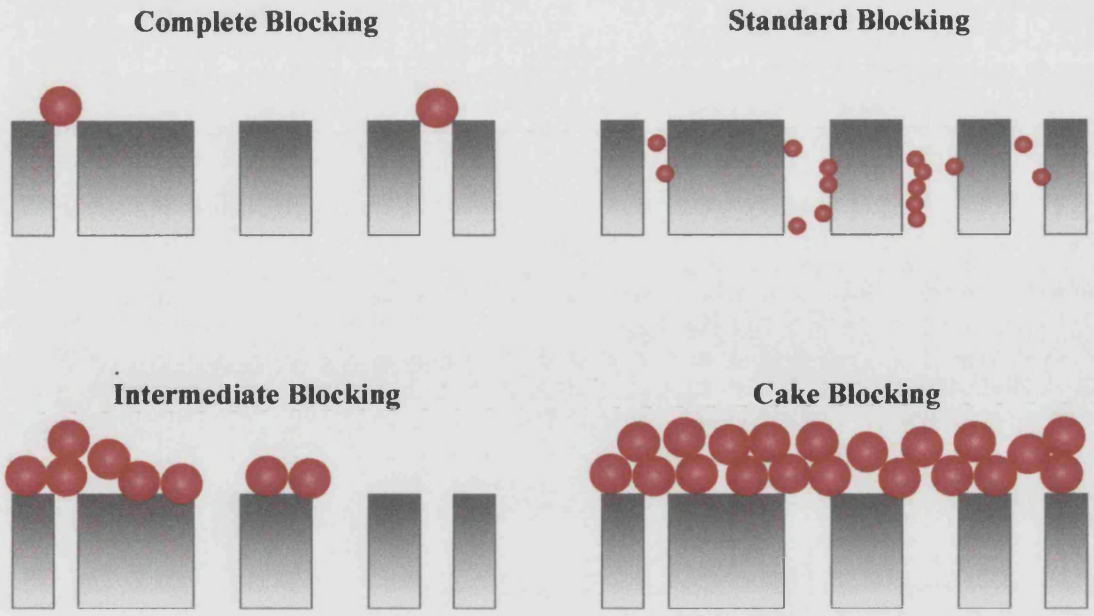



***Figure 2.8*** *Schematic diagram of fouling mechanisms for a multicomponent solution: complete, standard, intermediate and cake blocking mechanisms.*

Grace (1956) analysed the blocking laws in relation to the performance of the filter media to be used with particular reference to the standard blocking law. Hermia derived the intermediate blocking law and by 1982 had revised all the four blocking laws in a common frame of power law non-Newtonian fluids.

More recently Field *et al* (1995) extended these blocking laws to describe crossflow filtration by inclusion of a back diffusion term in the basic differential equation, as shown in Equation 2.15. By relating the flux ($J$) to the rate of flux decline/recovery ($dJ/dt$), the dominant mechanism i.e. cake, intermediate or complete blocking (Figure 2.8) can be established. The standard blocking mechanism involves deposition onto the internal pore walls and is not influenced by back diffusion from the membrane surface.

$$-\frac{dJ}{dt} = k\left(J - J^{*}\right)J^{(2-n)} \qquad \textbf{(2.15)}$$

Where $J^{*}$ is the flux at steady state, the constant, $k$, and the fouling index, $n$, taking different values depending on the fouling mechanism (i) cake (n=0), (ii)

intermediate blocking (n=1), (iii) standard (n=1.5), and complete blocking (n=2), mechanisms

Curve fitting of Equation 2.15 to experimental data will give an indication of the type of fouling occurring, and hence the extent and position of the deposition. This knowledge aids the implementation of the correct cleaning procedure.

## 2.2.4 Fouling Reduction

Under the worst circumstances fouling can cause a 95% reduction in membrane permeability compared to the initial flux observed with a clean membrane [Le (1982)]. Hence, manipulation of the factors that promote fouling is an important economic issue. Fouling reduction techniques are diverse, as each membrane separation requires its own specific treatment, although several approaches can be distinguished.

### *2.2.4.1 Membrane Surface Properties*

The nature of the membrane material, used for a particular separation, influences the interaction between the membrane and the process fluid. The membrane must be resistant to the pH, temperature and the chemical composition of the feed. The choice of correct membrane material is necessary to maximise compatibility and reduce fouling. As described in Section 2.1.1.4, altering the hydrophobicity or electrocharge of the membrane surface provides anti-fouling solutions. Precoating membranes either counteracts the deposition of protein on the membrane surface or prevents internal fouling which facilitates the cleaning process.

### *2.2.4.2 Pre-treatment of the Feed*

Fouling reduction often starts with the development of an appropriate pre-treatment method. Pre-filtration to remove particulates [Lee and Merson (1975)], centrifugation to remove fats [Tragardh (1989)] or chemical clarification [Daufin *et al* (1991)], reduces the fouling potential of the fluid. Ionic strength and pH adjustment have been shown to improve flux by up to 70% [Lee and Merson (1975)] and reduce membrane fouling [Heinemann *et al* (1989)]. Heat treatments such as pasteurisation, prior to filtration, are used to avoid biodegradation and contamination of the feed [Tragardh

(1989)]. While sequestering agents such as EDTA are often used counteract the insolubility of calcium salts.

### *2.2.4.3 Module Design*

Some modules are more susceptible to fouling than other designs. Module designs with small flow channels such as capillary fibres and spiral wound membrane modules are most likely to foul. The relative advantages and disadvantages of common designs are discussed in detail in Section 2.1.2. Whichever module design is used it should not promote fouling.

For a given module, the flow characteristics are very important. To minimise fouling, feed flow should be tangential to the membrane surface. To increase the mass transfer rate the flow should be changed from laminar to turbulent, if not directly by increasing the feed velocity along then, indirectly, by changing the module shape and dimensions (decreasing the module length or increasing the hydraulic diameter geometry).

Careful consideration should be given to the pressure distribution on the membrane. The feed solution may be over-pressurised near the inlet and under-pressurised at the outlet region, particularly in thin channel equipment. For optimum operation the pressure should be generally uniform and below the threshold pressure since over pressurised areas are liable to serious pore blockage.

### *2.2.4.4 Improved hydrodynamics*

A hydrodynamic approach to flux improvement is either by

**(i)** reduction of concentration polarisation by increasing the mass transfer away from the membrane

**(ii)** the lessening of fouling by increasing the wall shear rate

**(iii)** scouring the membrane surface

The mass transfer coefficient, k, can be reduced by changing the hydrodynamics of the system to reduce polarisation. The module shape and channel

dimensions can be varied and optimised to increase back diffusion of polarised species and reduce the build-up of solutes at the membrane surface.

The mass transfer coefficient, $k$, is related to the Sherwood number ($Sh$), by,

$$Sh = \frac{kd_h}{D} = a\,\mathrm{Re}^b\, Sc^c \qquad \textbf{(2.16)}$$

Where $Re$ is the Reynolds number, $Sc$ the Schmidt number, and $a$, $b$, and $c$ are constants.

$$\mathrm{Re} = \frac{d_h \upsilon}{\eta} = \frac{\rho \upsilon d_h}{\mu} \qquad \textbf{(2.17)}$$

$$Sc = \frac{\mu}{D} \qquad \textbf{(2.18)}$$

In these relationships, $\eta$ is the kinematic viscosity, $d_h$ the hydraulic diameter, $\mu$ the dynamic viscosity, $\rho$ the density, $\upsilon$ the flow velocity and $D$ the diffusion coefficient.

$$k = f(\upsilon, D) \qquad \textbf{(2.19)}$$

From equations (2.16-2.18) it can be seen that the mass transfer coefficient, $k$, is mainly a function of the diffusion coefficient and the crossflow velocity of the feed, as well as the viscosity and density of the permeate. The diffusivity of the solute can only be increased by changing the temperature. $k$ can be increased by increasing the feed velocity along the membrane or by making modifications to the flow channel.

Two different flow patterns can be distinguished, i.e. laminar and turbulent flow. A parabolic concentration profile can be observed over the whole cross-section for a fully developed laminar flow. For turbulent flow the velocity in the cross-section is constant and only in the boundary layer, near the wall, is the velocity lower. The Reynolds number, $Re$, is the measure of whether turbulent or laminar flow. For undisturbed flow through a straight pipe the change from laminar to turbulent flow

begins when the Reynolds number is greater than 2100. The semi-empirical relationships for mass transfer coefficients in pipes and slits are given in Table 2.4.

*Table 2.4* *Mass transfer coefficients in laminar and turbulent flow regimes*

| Channel | Laminar | Turbulent |
|---|---|---|
| Tube | $Sh = \frac{kd_h}{D} = 1.62\left(\mathrm{Re}\,Sc\frac{d_h}{l}\right)^{0.33}$ | $Sh = 0.04\,\mathrm{Re}^{0.75}\,Sc^{0.33}$ |
| Slit | $Sh = 1.85\left(\mathrm{Re}\,Sc\frac{D_h}{l}\right)^{0.33}$ | $Sh = 0.04\,\mathrm{Re}^{0.75}\,Sc^{0.33}$ |

Many attempts have been made to modify the hydrodynamic layer immediately above the membrane by transmembrane pressure pulsing. Bauser *et al* (1986) showed that applying a negative pulsatile pressure to the filtrate side of the module, during the ultrafiltration of protein solutions, gave a permanent flux improvement of about 50%. Rogers and Sparks (1991-1992) found that for the crossflow ultrafiltration of albumin solution transmembrane pressure pulsing improved permeate flux, for a low wall shear stress rate, to within 23% of the initial flux. The increase in flux, due to pulsing, was equivalent to that for a two hundred-fold increase in the crossflow rate for conventional laminar flow ultrafiltration. They found that pulsing did not improve flux values for turbulent flow.

For a given volumetric flowrate, the mass transfer coefficient can be maximised by increasing the shear rate. Modules operating in turbulent flow achieve this by using large recirculation rates, while in laminar flow modules this can be achieved by a reduced convective flux [Howell and Finnigan (1991)]. Da Costa *et al* (1993) improved mass transfer using spacers to reduce concentration polarisation with corrugated cellulose acetate membranes. Bellhouse and co-workers developed the concept of dimpled membranes over which the fluid is pulsed [Stairmand and Bellhouse (1985)]. This created vortices that were swept away from the membrane surface following flow reversal, simulating the action in blood vessels. Colman and Mitchell (1991) increased flux in a UF membrane system by a factor of three by the introduction of vortex mixing in baffled channels. Extensive work on the effect of both

steady and pulsatile flow with baffles to increase local mass transfer, by promoting turbulence and interrupting the development of the boundary layer, has been carried out [Howell and Finnegan (1991)]. Belfort (1989) has described how frequent flow reversal reduces the build-up of foulants at the entrance region of the module by changing the entrance position. Recent work by Wright *et al* (1994) and Bellara *et al* (1996) has used controlled gas sparging to increase the mass transfer coefficient and enhance flux.

### *2.2.4.5 Cleaning*

The choice of cleaning method depends on the module configuration, membrane structure and material, as well as the type of foulant encountered. There are 3 principle methods of cleaning.

#### 2.2.4.5.1 Hydraulic Cleaning

Pressure release techniques allow the relaxation of the fouling layer. They have traditionally been used in reverse osmosis systems where the operating pressure differentials are higher [Lahiere and Goodboy (1993)]. The feed pressure is released and the direction of the permeate reversed in order to remove fouling from within the membrane pores or at the membrane surface.

Backflushing, as depicted in Figure 2.9 [Mulder (1991)], is only applicable in membranes where the structure is capable of withstanding the pressures employed to induce flow [Padilla-Zakour and McLellan (1993)]. This technique has found particular favour within the beverage industry where the use of tubular ceramic membranes is widespread [Gan and Howell (1994)]. A variation of traditional backflushing is transmembrane pressure pulsing [Rogers and Sparks (1991-92)], or "back-shock" where the backpressure is applied with an extremely rapid pulse [Wenten *et al* (1994)].

Partial backflushing can be achieved by fluid recycling. The permeate ports are shut off and the process stream recycled through the feed side of the module. Thus, permeate flows through the membrane from the feed side but in the reverse direction, thereby backflushing the membrane at the outlet and removing loosely adhered material. Recycling can be used during production by cutting off the permeate flows

for short periods of time. However, cleaning agents rather than permeate are ultimately required [Leaver and Melling (1987)].

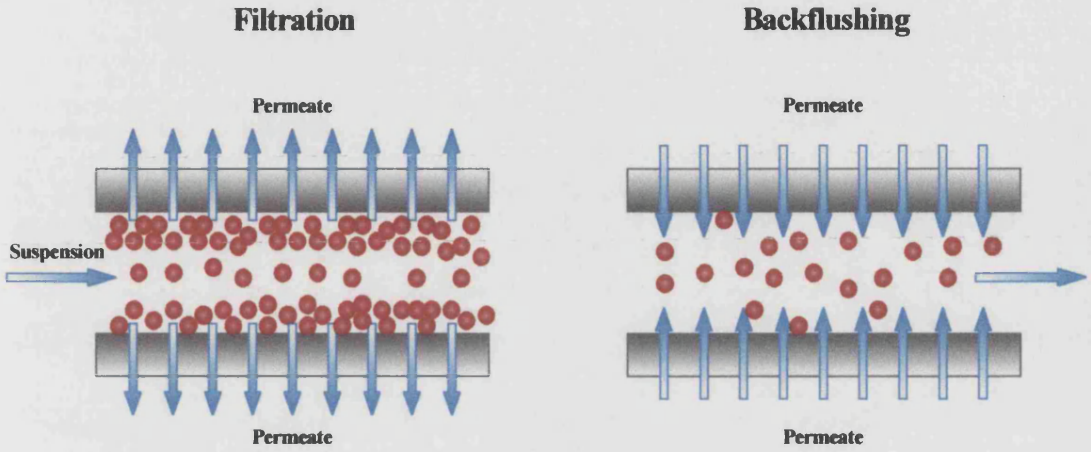



***Figure 2.9*** *The principles of backflushing*

#### 2.2.4.5.2 Mechanical Cleaning

Improvements to the hydrodynamics of the membrane system not only reduce fouling but should also reduce costs because of decreased power consumption. Crossflow operation is preferred because the washing action of the fluid passing tangential to the surface of the membrane decreases the redeposition of the fouling material. Rotating cylindrical filters can be used, where the fouling layer is swept away. Pulsatile flow, and the use of baffles may also be used to improve cleaning regimes (Section 2.2.4.4).

Lowe and Durkee (1971) achieved a three-fold flux improvement by using plastic spheres moving randomly in the flow channels during reverse osmosis of orange juice. Tzeng and Zall (1990) used the mechanical scrubbing effects of polymers to enhance flux recovery. Other researchers have used water droplets carried by a high-speed air stream to scour the membrane surface to improve and shorten cleaning procedures.

The use of pulsed electric fields, for the physical cleaning of cellulose nitrate MF membranes, showed a ten-fold increase in the permeation rate when applied throughout the separation, on a periodic basis [Bowen *et al* (1989)]. Using the same technique, Robinson *et al* (1993) showed a 25-40% decrease in solute related resistance to the permeation rate for concentrating proteins using UF.

Wakeman and Tarleton (1991) have also developed ultrasonic fields for the successful reduction of fouling.

#### 2.2.4.5.3 Chemical Cleaning

The most important industrial method for deposit removal is chemical action. A number of chemicals are used separately or in combination (Section 2.3). The nature of the deposit is significant to the choice of cleaning chemicals. It is important that the chemicals are membrane compatible. As is the concentration of the chemicals used and the cleaning time. Whilst most of the foulants can be removed by the appropriate cleaning action, the action itself compromises the intrinsic membrane functionality and lifetime (Section 2.1).

## 2.3 THE CLEANING PROCESS

The cleaning process must remove deposits and restore the permeability and selectivity of the membrane. Chemical cleaning is the only viable proposition for the removal of proteinaceous deposits from most flatsheet, MF membrane systems [Mulder (1991)]. The factors which affect deposit removal, and hence flux recovery, are assessed in this section. The mechanisms of flux recovery are discussed and the development of cleaning models reviewed.

### 2.3.1 Engineering Considerations for Chemical Cleaning

In discussing the engineering aspects of cleaning fouled microfiltration membrane systems, three phases have to be considered:

(i) **A solid phase** - the membrane surface (and pores).

(ii) **An adherent soil phase** - the deposit.

(iii) **A liquid phase** - the cleaning solution.

Plett (1985) described cleaning as a heterogeneous reaction between the cleaning solution and the deposited layer. As summarised by Bird (1993), cleaning can be considered a multi step process:

(i) The diffusion of cleaning solution to the surface.

(ii) Wetting of the surface i.e. contact between the cleaning solution and the deposit.

(iii) Penetration of the cleaning solution into the deposit.

(iv) Reaction between the cleaning solution and the deposit.

(v) Removal of the deposit.

Difficulties in any one of these stages, such as poor mass transfer in the low shear stress areas of the membrane module, low diffusivity of cleaning chemicals through compacted deposits or slow reactions, can be the rate-determining step.

Steps (i) and (v) depend on the external mass transfer i.e. the velocity of the cleaning solution. Step (iii) depends upon internal diffusion, so the transport properties of the cleaning solution, as well as the nature of the deposit, is important. Steps (ii) and (iv) depend on the deposit and cleaning solution chemistry.

### 2.3.2 Cleaning Conditions

Optimising the cleaning process requires knowledge of how the chemical, thermal and hydraulic operating conditions effect cleaning. Research has shown that the time taken to clean is a function of the cleaning agent, its concentration, temperature, flowrate and transmembrane pressure.

#### *2.3.3.1 Cleaning Chemicals*

Chemical cleaning agents work by a number of different mechanisms including chemical modification, solubilisation and/or displacement of the foulants from the membrane. Tragardh (1989) maintained that the chemicals used should loosen and dissolve the foulants while keeping them dispersed in the solution. It is important that the cleaning agent should not provide a new fouling source and it should not degrade the membrane or auxiliary equipment.

Not only is the cleaning ability of the chemical agent important but also factors such as [Kane and Middlemass (1985)]:

- High active component concentration.
- Good solubility.
- Moderate foam levels.
- Good buffer system.
- Good chemical stability.
- Disinfection of all wetted surfaces.
- Cost
- Safety

The chemicals used may be simple or a cocktail of components. A large number of proprietary cleaning solutions have been developed for specific applications.

- **Alkalis**

  By acting as dispersants, alkalis can solubilise carbonates, bind ion salts, regulate pH, emulsify fat and peptise proteins. Phosphates and polyphosphates have a moderate cleaning effect. But sodium hydroxide has wide spread use as an industrial cleaning agent and forms the basis of most commercial dairy cleaning products where it is effectively used to saponificate fat and solubilise protein [Leaver and Melling (1987)].

- **Acids**

  Mineral or organic acids such as nitric, phosphoric, oxalic and citric acid are effective at removing inorganic salts formed by calcium or metal oxide films. Acid such as HCl are corrosive, and care should be taken with their use on stainless steel process equipment

- **Surface Active Agents (surfactants)**

  Wettability and rinsability are improved by altering the surface tension. Improved contact between the cleaning chemicals and deposit minimise the amount of water and chemicals used and the length of rinsing time required [Giese (1991)]. Surface active agents maybe anionic, cationic, non-ionic or amphoteric [Tragardh (1991)].

(i) **Anionic** agents are neutral organic foaming agents e.g. soap, alkyl sulphate, alkyl sulphonate.

(ii) **Cationic** agents consist of quaternary ammonium compounds. Less effective than other agents, their use in the dairy industry is not recommended as they can prohibit the growth of cultures used.

(iii) **Non-ionic** agents are condensation products such as ethylene oxide. They are low foaming, independent of pH and easy to rinse off, but are less effective than anionic agents [Tragardh (1989)].

Great care has to be taken when introducing surfactants and other surface agents into a membrane plant, as they may be absorbed on to the membrane surface resulting in a flux decline or permanent damage [Yamagiwa (1993)]. Many studies have shown these amphoteric substances also affect the ease of cleaning [Le and Howell (1983), Luss (1984), Chen (1992), Yamagiwa (1993), Akay and Wakeman (1995), Fudge (1995)]. This is due to their specific abilities to form aggregates in the form of micelles.

- **Chelating Agents (sequestrants)**.

  Citrate, sodium tripolyphosphate, tetrapotassium pyrophosphate, sodium gluconate and ethylene diamine tetracetic acid (EDTA) are common chelating agents which combine with metal ions to form soluble complexes to prevent scale deposition [Giese (1991)]. The environmental aspects of using EDTA, and complex phosphate based cleaning agents, in single stage cleaners is, questionable, due to their complexing properties with heavy metals, such as those found in sewage treatment processes [Grashoff (1989)].

- **Enzyme Detergents**

  Particularly useful with membrane materials which are sensitive to pH and temperature, such as cellulosic polymers [Harper and Moody (1981)]. Enzymes have good dispersion and emulsifying effects, even at low

temperatures. However, they are costly to produce, stabilise and formulate into effective detergents [Kane and Middlemass (1985)]. They are slow compared to conventional chemical cleaning agents and therefore cleaning time is increased. The development of enzyme detergents from thermophilic bacteria will increase their stability over a greater range of pH and temperature [Coolbear *et al* (1992)]. Nevertheless, there is still concern that residual enzyme activity can affect the quality of cultures used in the dairy industry and food products.

- **Sanitisers**

Disinfection destroys all pathogenic micro-organisms and reduces the numbers of others. This crucial procedure is the final step in the cleaning operation.

Chemicals used for sanitation include oxidising agents such as hydrogen peroxide and sodium hypochlorite. When added to sodium hydroxide, sodium hypochlorite also has some cleaning ability [Daufin *et al* (1991 - 1993)]. Sodium bisulphate has been used for disinfection, but has been shown to corrode stainless steel [Smith and Bradley (1986)]. Sodium hydroxide itself acts as a disinfectant and its use means that further disinfection is unnecessary [Leaver and Melling (1987)].

- **Water**

Water acts as a carrier for cleaning solutions and sanitisers. Clean water rinsing also provides essential steps in the cleaning regime.

Water quality is of great importance in membrane processes. Hardness is responsible for mineral deposits, undesirable films, precipitates and excessive detergent consumption [Giese (1991)]. Therefore, pre-treatment of process water is an essential procedure for membrane processes. Standards for water hardness and quality [afterTragardh (1989)], are listed in Table 2.5. The effect of water quality on the fouling and cleaning of membranes, due to the influence of mineral deposition, has been discussed in more detail by Armishaw (1982), Tragardh (1989) and Giese (1991).

*Table 2.5 Water quality standards for membrane cleaning processes*

| Property | Specification |
|---|---|
| pH | 6-8 |
| Total Dissolved Solids | < 500 mg/l |
| Hardness | <200 mg/l |
| Iron | < 0.2 mg/l |
| Manganese | < 0.1 mg/l |
| Chlorides | 20 mg/l |
| Silicate | < 15 mg/1 |
| Total Plate Count | < 1000 per ml |
| Coli Count | < 0.001 per ml |

### *2.3.3.2 Concentration*

It has generally been assumed that increasing the concentration of the cleaner will increase deposit removal. However, there is a concentration beyond which no further increase in the rate of deposit removal will be observed. Conflicting results indicate that the use of concentrations beyond this level may result in detergent saturation or decreased cleaning ability [Smith (1990)].

Several studies have shown that cleaning agents alkalis and acids do not have this concentration plateau. Early studies indicated that the time to clean was dependent on the concentration of the cleaning agent [Parkin and Marshall (1976)]. Tzeng and Zall (1990) found that the optimum concentration for cleaning a ceramic UF membrane was dependent on the deposit composition. It was determined, through the regression analysis of their experimental results, that sodium hydroxide concentrations of 0.8 wt.% for whole milk and 1.0 wt.% for skim milk would give the greatest flux recovery. Shorrock and Bird (1998) found that a sodium hydroxide concentration of 0.01 wt.% gave the greatest flux recovery for the removal of a proteinaceous matrix formed during yeast filtration using PES MF membranes.

An optimum sodium hydroxide concentration of 0.5 wt.% was found to minimise cleaning time for both WPC and milk deposits from stainless steel surfaces [Bird and Fryer (1991-1992), Bird (1993)]. Visualisation of the cleaning process

showed that on contact with caustic based cleaning agents the deposit swells, transforming it into a more open structure of high voidage. At the optimum cleaning agent concentration it was more susceptible to removal by fluid mechanical shear forces.

### *2.3.3.3 Temperature*

With the exception of the use of enzymes as cleaning agents, it is generally assumed that any increase in temperature will aid the cleaning process.

Cleaning solution viscosity decreases with an increase in temperature and consequently the Reynolds number increases. The diffusion coefficients and reaction rates should both increase which would assist deposit breakdown and dissolution of organic foulants. Jennings (1965) stated that an increase in temperature continued to increase cleaning efficiency until a point where the detergent decomposed or the vapour pressure of the cleaning solution interfered. The work of Bird [Bird and Fryer (1991), (1992), Bird (1993)] found that increasing cleaning temperatures up to 70° reduced cleaning times for the removal of whey proteins from stainless steel. A reduction in cleaning times has implications for the cost of the cleaning operation which have to be balanced against the additional costs incurred by heating cleaning solutions and the temperature compatibility of process equipment.

Hard surface cleaning work has assumed an Arrhenius relationship between deposit removal and cleaning temperature.

$$r = A.e^{(-E_A/RT)} \qquad \textbf{(2.20)}$$

Where $r$ is the removal rate, $E_A$ is the activation energy, $A$ is the pre-exponential factor, $R$ is the gas constant and $T$ is the absolute temperature

Gallot-Lavallée and Lalande (1985) and Perlat (1986) found the overall sensitivity of the cleaning reaction to temperature was situated between the activation energy of the diffusion process (10 - 25 KJ/mol) and that of chemical reactions (150 - 300KJ/mol). Physiochemical transformations and thermal degradation of the deposit, which may overlap the cleaning process, would not be explained by Arrhenius kinetics

### 2.3.3.4 *Crossflow Velocity (CFV)*

The influence of flow parameters is often referred to as the mechanical effect. The scouring action of the fluid passing tangentially across the surface removes loosely bound material. For hard surfaces it has been shown that as low fluid velocities increased so did the cleaning rate, and consequently, the time required to clean the surface decreased [Bird (1993)]. Increasing the fluid velocity represents a means of inputting energy into the system and investigating deposit removal with turbulent flow regimes (Reynolds number > 4000) has been of particular interest.

For membrane systems the cleaning rate is higher during the initial stages within a turbulent flow regime but there is little improvement in the final flux recovery. Mackley and Sherman (1994) have shown that removal of deposit was dependent on the deposit thickness and that where greater shear forces are used a the thinner layer resulted which provided a greater resistance to flow through the membrane than a thicker, less compacted, layer.

Several researchers have suggested that for a defined cleaning time laminar flow is likely to be more economical, due to the reduced pumping costs required to achieve the desired flux recovery.

### 2.3.3.5 *Transmembrane Pressure (TMP)*

As described in Section 2.2.1, the total hydraulic resistance to mass transfer in a membrane system ($R_T$) is directly proportional to the applied or transmembrane pressure.

$$R_T = \frac{\Delta P}{\mu J_v} \qquad \textbf{where} \qquad \Delta P = \frac{(P_i - P_o)}{2} - P_p \qquad \textbf{(2.21)}$$

$\Delta P$ is the pressure differential, $P_i$ is the inlet pressure, $P_o$ is the outlet pressure and $P_p$ the permeate pressure

The application of a positive TMP gradient during any cleaning procedure allows the collection of kinetic data for evaluation. However, experimental investigations by Parkin and Marshall (1976) and Kim *et al* (1993) advise that zero pressure should be applied to the membrane during the initial stages of the cleaning

procedure. Pressure release should inhibit compaction effects, making the removal of loosely bound surface material easier.

### 2.3.4 Methods for Evaluating Cleaning

A quantitative measurement of cleaning efficiency determines the validity of all the results and conclusions subsequently derived. The chosen measurement technique must provide accurate cleaning kinetics, as opposed to a final value, if the mechanisms of cleaning are to be elucidated.

Visual inspection includes methods such as direct observation of wet and dry surfaces, checking for discoloration and wettability measurements. The major limitation of these traditional methods is the individual's ability to detect residual deposit. In addition, this method is often not practical for evaluating surfaces in a closed system.

Spectroscopic analysis of membrane surfaces is a common analytical technique. X-ray photoelectron spectroscopy of the fouling layers before and after each cleaning step allowed Daufin *et al* (1991-1992) to collect information about the depth of deposit and an elementary comparison to be made of deposits that remained after cleaning procedures. Chemical analysis of the membrane can provide valuable information. Bartlett (1996) used Fourier Transform Infrared Spectroscopy (FTIR) to shown that the adsorption of proteins to polymeric UF membranes. The use of cleaning agents such as surfactants [Yamagiwa *et al* (1994)], sodium hydroxide, oxalic acid and formulated cleaning compounds [Nystrom and Zhu (1996)] caused irreversible chemical changes to membrane surfaces. This suggests that a used surface can never be cleaned to its original or pristine condition.

Bohner and Bradley (1992) determined the stability of polysulphone UF membranes by chemically analysing whey and permeate samples, taken before and after each cleaning procedure. They used the micro-Kjedahl technique for measuring the retention of nitrogen as a method for assessing the physical damage caused by hot cleaning solutions.

Optical measurements use the transmission, reflection, absorbance or scattering of light to indicate the presence of soil. Daufin *et al* (1991-1992) tested the permeate solution from cleaning experiments for calcium using atomic adsorption, and protein by

using a 280 nm wavelength absorbance. The direct measurement of protein, by the absorption of UV light at 280 nm, gave a kinetic profile of BSA and α-LA concentrations, during the cleaning of polyethersulphone UF membranes using a dead-end Amicon module [Bartlett (1996)]. The technique was accurate, simple to use and required only equipment which is routinely used in any laboratory. The application of the colourimetric BIO-RAD Micro-Assay also showed promise as a technique for the detection of low protein concentrations.

Gravimetric methods use the amount of soil remaining on surfaces to indicate the presence of fouling. The dry weight of the test piece is determined before fouling and after cleaning with the difference in weights indicating the amount of deposit remaining. This method is generally impractical in process situations but can be useful in laboratory evaluations were it is often used to determine hard surface cleaning kinetics.

For MF membranes it is generally perceived that the magnitude of deposit removed is not proportional to the functionality of the system. The location of the fouling and type of foulant are equally important. Generally, the effectiveness of a cleaning procedure is checked by measuring the water flux after cleaning at defined pressure, temperature and fluid velocity. Whilst a good water flux does not guarantee a good operational flux a low water flux does indicate that cleaning was insufficient. The product flux in the following run may be a better indicator of a satisfactory cleaning procedure.

### 2.3.5 Cleaning Mechanisms and Models

The study of cleaning dynamics can predict the necessary time, and the operating conditions, required to achieve the desired level of cleanliness. To calculate them it is necessary to develop mathematical models. Ideally, known parameters should be used, but unknown parameters may be fitted through regression analysis of the experimental results. However, the reliability of the model depends on how closely it represents the mechanisms involved. To date, there has been little published information that describes the mechanisms of the membrane cleaning process, and few models developed.

Tzeng and Zall (1990) evaluated the thermal, chemical and hydraulic conditions used to clean hollowfibre polysulphone membranes fouled during the processing of whole and skim milk solutions. A mechanism was postulated to account for the flux recovery behaviour found experimentally during sodium hydroxide cleaning and the subsequent rinsing procedure. The results are shown in Figure 2.10.

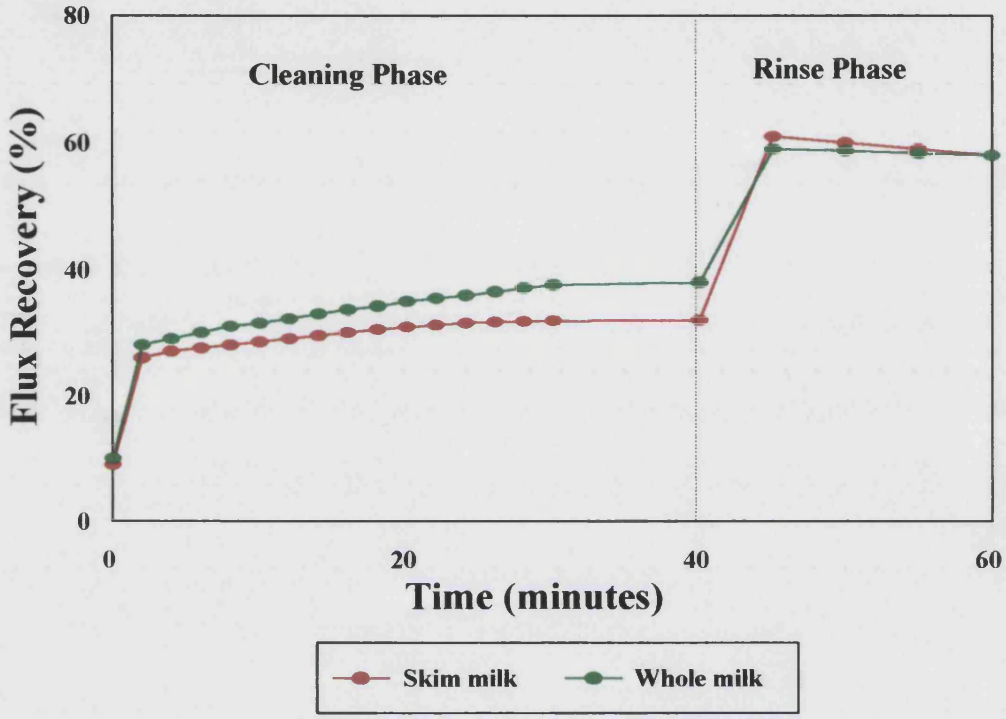



***Figure 2.10*** *Typical flux recovery curves for the cleaning of PS membranes fouled during milk processing at 105°F. Cleaned with 0.5 wt.% NaOH at 125°F, 15 lb.f.in$^{-2}$ [Tzeng and Zall (1990)].*

They classified the foulants were into three species

- **Species One** was readily solubilised on contact with sodium hydroxide and was quickly removed resulting in a sharp flux recovery during the first few minutes of cleaning.

- **Species Two** was not removed but reacted with sodium hydroxide to form a new foulant. The new foulant had similar permeation characteristics as the

original deposit. Only a small increase in flux recovery was observed during the next ten minutes of cleaning. It was evident from the second sharp increase in the flux recovery rate that the new foulants were easily rinsed off with water.

- **Species Three** was more resistant to cleaning with sodium hydroxide and remained on the surface of the membrane.

Experimental results suggest that the transformation of Species Two into new water removable foulants was accomplished within 20 minutes and that flux recovery was not improved by prolonging the cleaning time. This agrees with Bourne and Jennings (1968) theory that the conversion of 'hard-to-clean-deposit' into 'easy-to-clean-deposit' had the greatest potential for an improvement in cleaning efficiency.

Through regression analysis of their experimental results Tzeng and Zall (1990) concluded that concentration ($C$), temperature ($T$) and transmembrane pressure ($P$) affected the flux recovery characteristics of whole and skim milk differently.

**For whole milk**

$$\%FR = -21.2 + 0.567T + 52.8C - 33.1C^2 \qquad \textbf{(2.22)}$$

**For skim milk**

$$\%FR = 562 + 9.94T + 63.3C + 5.7P - 0.0444T^2 - 31.3C^2 - 0.19P^2 \qquad \textbf{(2.23)}$$

Quadratic terms with negative coefficients indicate the existence of optimal conditions for flux restoration. The optimum conditions for the flux restoration of the membranes fouled with skim milk were given as 112°F using a transmembrane pressure of 15 lb.f.in$^{-2}$ with a 1.0 wt.% sodium hydroxide solution. For membranes fouled with whole milk the maximum flux recovery was found to be independent of transmembrane pressure, but proportional to temperature, when using an optimum concentration of 0.8 wt.% sodium hydroxide. This analysis suggested that the mechanisms of flux recovery for membranes fouled with skim or whole milk deposits

were dissimilar. These results demonstrate that the foulant and fouling conditions need to be characterised to assess cleanability.

Daufin *et al* (1992) reported the removal of milk deposits from a ceramic tubular UF membrane using caustic based cleaning agents. By measuring the hydraulic resistance they found that the decrease in residual fouling during cleaning, $R_c$ fitted the kinetic second order law

$$\frac{dR_c}{dt} = -kR_c^2 \qquad \textbf{i.e.} \qquad \frac{1}{R_c} = kt + C \qquad \textbf{(2.24)}$$

This correlation showed that the removal of resistance during cleaning was dependent on the fouled state of the membrane and the detergent composition. However, neither the true reaction rate nor the mechanisms of deposit removal were obtained from this kinetic observation.

As reviewed by Plett (1985), many hard surface-cleaning models suggest zero or first order models for both deposit removal and/or cleaning agent concentration. Gallott-Lavalle and Lalande (1985) developed an important multistage mechanistic model which suggested an intermediate 'swollen-deposit' phase. The cleaning process was divided into four stages, each stage being represented by a first order differential equation. Several researchers have used this as a basis for developing models which describe the removal of whey protein deposits from stainless steel surfaces [Perlat (1986), Bird and Fryer (1992), Bird (1993)].

Bird [Bird and Fryer (1992), Bird (1993)] presented a kinetic model to describe the diffusion and reaction in a deposit of initial thickness $\delta$, which can be considered as two layers (Figure 2.11). The upper layer of swelled deposit has a thickness of $\delta y \chi$ which can be removed. The lower layer of deposit, of thickness $\delta x$, is not yet removable. $\chi$ is the ratio of swollen to unswollen deposit thickness. This swelling factor, $\chi$, was measured by visualisation of the deposit to be 2.5.

The equations governing the rate of change in thickness of these two layers were expressed as:

$$\frac{d(\delta x)}{dt} = k_0 \qquad \textbf{(2.25)}$$

$$\frac{d(\delta y\chi)}{dt} = k_0 - k_1 \delta y\chi \qquad (2.26)$$

Rearranged to give

$$\frac{dy}{dt} = \frac{k_0}{\delta\chi} - k_1 y \qquad (2.27)$$

The rate of change of removable deposit to non-removable deposit was constant and the rate of loosing the removable deposit was proportional to the thickness of that deposit.

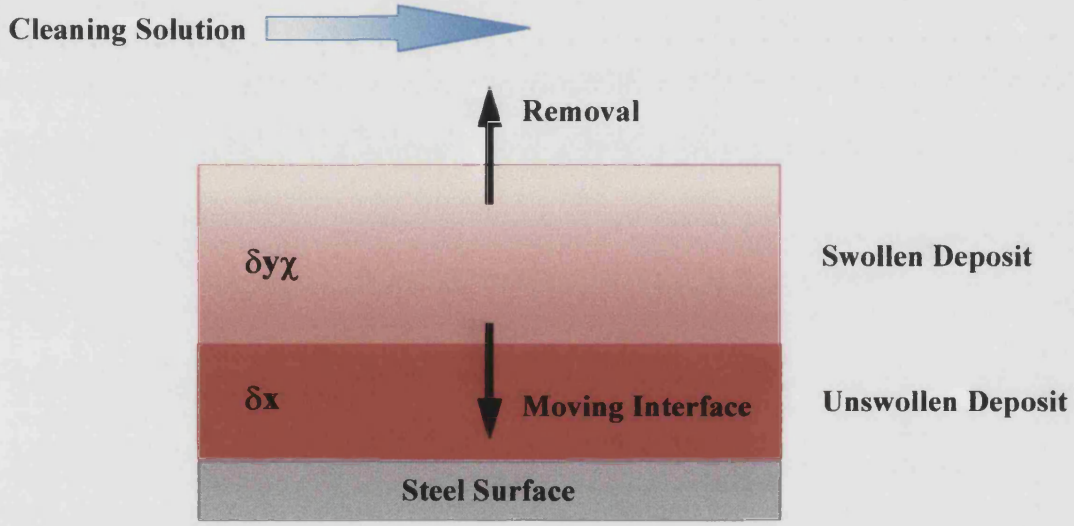



***Figure 2.11*** *System arrangement for swelling model [Bird (1993)]*

Although the model represents a simplification of the processes that occur during the removal of proteinaceous deposits from hard surfaces, it gave curves of a similar shape to those found experimentally. While both the initial rate of increase in the cleaning rate and the overall cleaning time were functions of both kinetic processes some parts of the curve were functions of only one kinetic process:

(i) the time to reach the maximum cleaning rate was dependent on the time required to convert all the deposit to a removable form i.e. on $k_0$ only

(ii) the drop from the peak removal rate depended on the removal process i.e. $k_1$.

Therefore, it has limited use in characterising cleaning as the mechanisms aren't clear.

## 2.4 CONCLUSIONS

The cleaning of fouled membrane systems is highly complex. However, in light of the literature reviewed in this chapter, the factors that affect the cleaning process can now be assessed:

(i) **The membrane process**. MF systems are important technologies for the processing of complex biological fluids. A greater understanding of the process parameters that compromise membrane functionality, and limit the membrane's lifetime, enhances the practicality of using these membrane processes..

Cleaning studies must be conducted in a system with defined process parameters. Process features such as membrane materials and system design must be characterised in order to obtain reliable information on the membrane process. As many variables as possible should remain constant so that the acquisition of data should be accurate and reproducible.

(ii) **The fouling process**. Given the complex nature of biological solutions MF processes are habitually fouled during processing. Characterising the fouling problem is prerequisite to any cleaning study. The nature of the fouling problem plays an important role in determining the ease of deposit removal. Fouling must be carried out under defined conditions that ensure that a sufficiently severe and reproducible deposit is generated, so that cleaning experiments can be evaluated.

(iii) **The cleaning process**. The cleaning process must remove deposits and restore the permeability and selectivity of the membrane. In most cases chemical cleaning is the only viable proposition for the removal of proteinaceous

deposits from flatsheet, MF membranes. Research has shown that the time to clean is a function of the cleaning agent, its concentration, temperature, crossflow rate and transmembrane pressure. Optimising the cleaning process requires the generation of kinetic data using controlled chemical, thermal and hydrodynamic conditions, so that the mechanisms of flux recovery can be elucidated and models developed which describe the experimental results.

Consideration of the available literature has identified the key process and design parameters required for the kinetic study of membrane cleaning. This has led to the development of a an experimental system for the fouling and cleaning of flatsheet, MF membranes which is representative of an industrially relevant problem.

# CHAPTER 3

# AN EXPERIMENTAL CLEANING SYSTEM

## 3.0 INTRODUCTION

A review of the available literature has identified the key process and design considerations for studying membrane cleaning. This chapter presents an experimental system for the cleaning of MF membranes fouled with a reconstituted Whey Protein Concentrate (WPC) solution.

The material properties of the system are classified and their functional parameters identified. The quantitative, qualitative and mathematical analysis techniques utilised in this study are then described. Experimental equipment has been designed and constructed to produce fouled membrane samples from a fully defined system. The fouled membranes are then cleaned, *in-situ*, under controlled thermo-hydraulic conditions. Protocols have been constructed which visualise the cleaning process and provide comparative, kinetic, cleaning data. These protocols are assessed and the inherent errors analysed.

The experimental results provide information to elucidate the mechanisms of chemical cleaning and aid the development of a mathematical model.

## 3.1 MATERIAL CLASSIFICATION

### 3.1.1 Membranes

As detailed in Table 3.1, the three types of flat-sheet, microfiltration membrane utilised in this study, aim to be representative of the diverse material and structural properties available. This allows the cleaning data generated to be assessed as generic cleaning phenomena or membrane specific.

#### *3.1.1.1 Sintered Stainless Membrane*

Sintered stainless steel MF membranes with a nominal pore size of 2 μm were supplied by Pall Process Filtration Ltd (Grade M020). The membranes, shown in Figures 3.1a and 3.1b were formed by a process of laying 316 low carbon stainless steel powder

within the pore structure of a stainless steel wire mesh and sintering the material [Crane (1992)]. This process produced a rigid membrane, with a nodular structure of high physical resistance and chemical compatibility with caustic cleaning solutions.

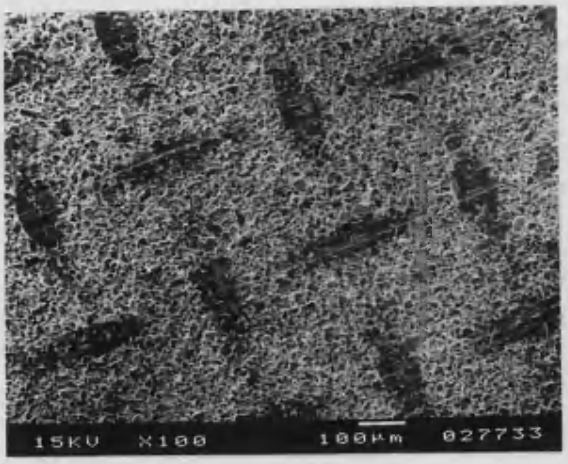



***Figure 3.1a*** *Top view of the sintered stainless steel membrane*

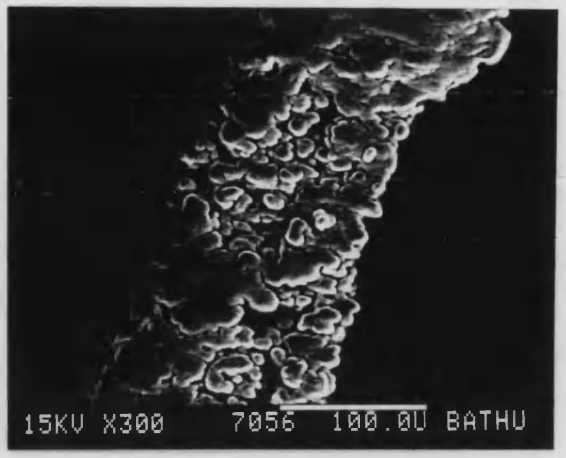



***Figure 3.1b*** *Cross-sectional view of the sintered stainless steel membrane*

### *3.1.1.2 Ceramic Membrane*


***Figure 3.2a*** *Top view of the ceramic membrane*

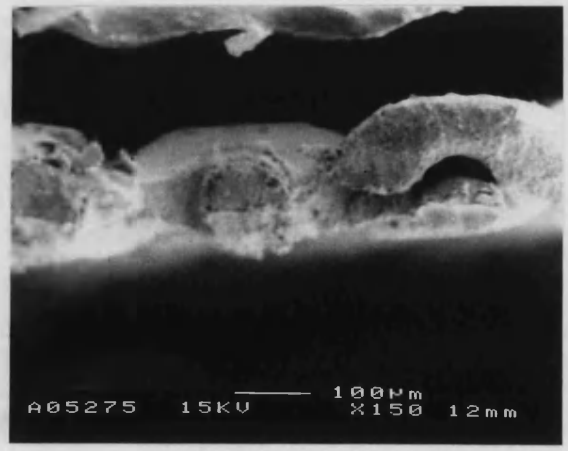



***Figure 3.2b*** *Cross-sectional view of the ceramic membrane*

The 0.1 μm ceramic membranes supplied by NWW Acumem Ltd, were prepared by dipping a nickel and aluminium alloy (Icontel™) mesh into a ceramic slurry which was allowed to air dry. This procedure was repeated 3 times before firing the membrane in air [Baird (1993)]. This produced a semi-rigid, symmetric membrane with a nodular, structure (Figures 3.2a and 3.2b). The membrane had a porosity of only 18% which was reflected in the relatively low water flux.

### *3.1.1.3 Polyethersulphone (PES) Membrane*

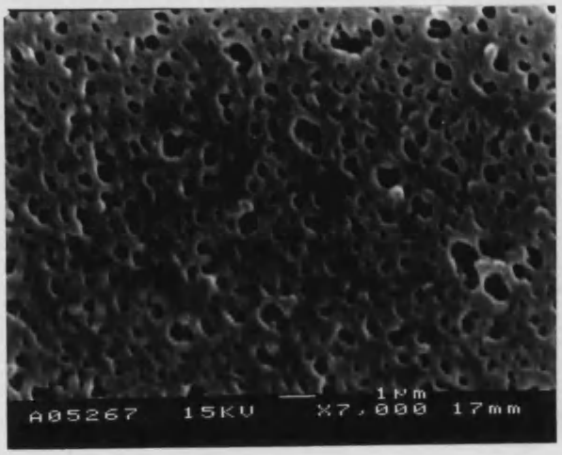



***Figure 3.3a*** *Top view of the PES membrane*

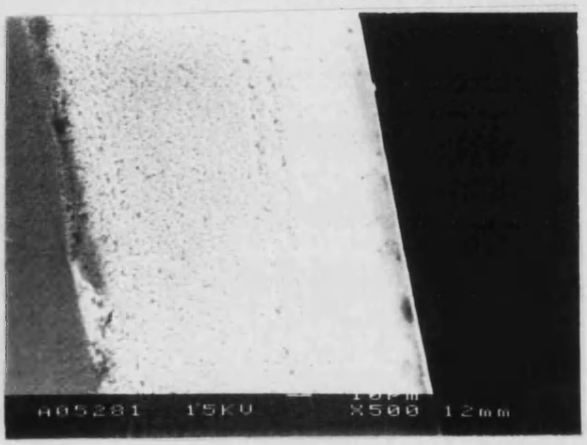



***Figure 3.3b*** *Cross-sectional view of the PES membrane*

***Figure 3.3c*** *Expanded cross-sectional view of the PES membrane*

The Supor 100™ polyethersulphone (PES) membranes were supplied by Gelman Sciences as having the retention characteristics of a 0.1 μm MF membrane. However, subsequent data from the supplier gave a pore size distribution of 1.75 - 2.1 μm. SEM's of the membrane show a composite membrane structure with a total thickness of 150 μm (Figures 3.3a-c).

*Table 3.1* *Chemical and physical characteristics of test membranes*

| Material | Sintered Stainless Steel | Ceramic (Zirconium Oxide) | Polyethersulphone (PES) |
|---|---|---|---|
| **Nominal Pore size** | 2 μm | 0.08 - 1.5 μm (mean 1.0 μm) | 1.75 -2.1 μm |
| **Porosity** | 25 % | 18 % | 60 % |
| **Pristine Water Flux (50°C, 1.59 $ms^{-1}$)** | ≈ 2800 $kg.h^{-1}.m^2.bar^{-1}$ | ≈ 1100 $kg.h^{-1}.m^2.bar^{-1}$ | ≈ 1200 $kg.h^{-1}.m^2.bar^{-1}$ |
| **Active Layer Thickness** | 150 μm | 100 - 150 μm | 50 μm |
| **Structure** | nodular symmetric | nodular symmetric | composite |

## 3.1.2 Chemicals

Important properties such as composition, density and viscosity were determined for the chemicals utilised in this study. The density variation with temperature and concentration was determined by using a Gay-Lussac pyknometer in accordance with BS 733 (1987). The viscosity of the test chemicals was determined in accordance with BS 188 (1977). Refer to Appendix I for details.

### *3.1.2.1 Water Quality*

The City of Bath is in a hard water area where tap water contains between 200 - 400 ppm calcium [Carver (1993)]. For the purpose of this study, distilled water with less than 20 ppm calcium [Carver (1993)] was used as rinse water and to make up all process solutions. A linear decrease in density was observed with increasing temperature

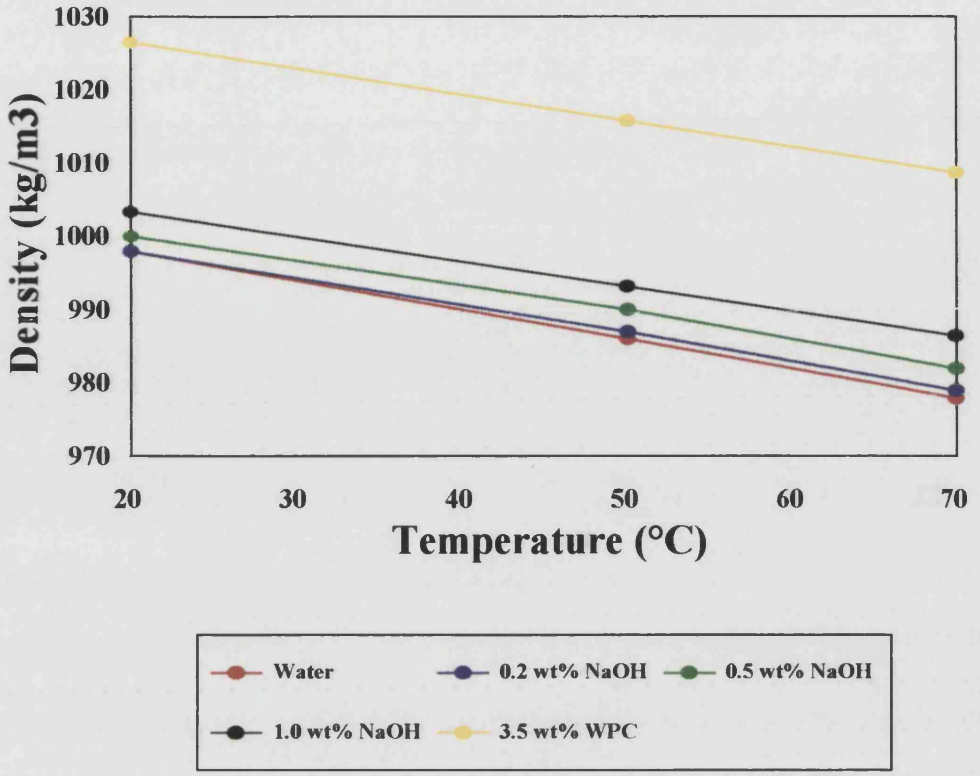



***Figure 3.4a*** *Density variation with temperature for test solutions*

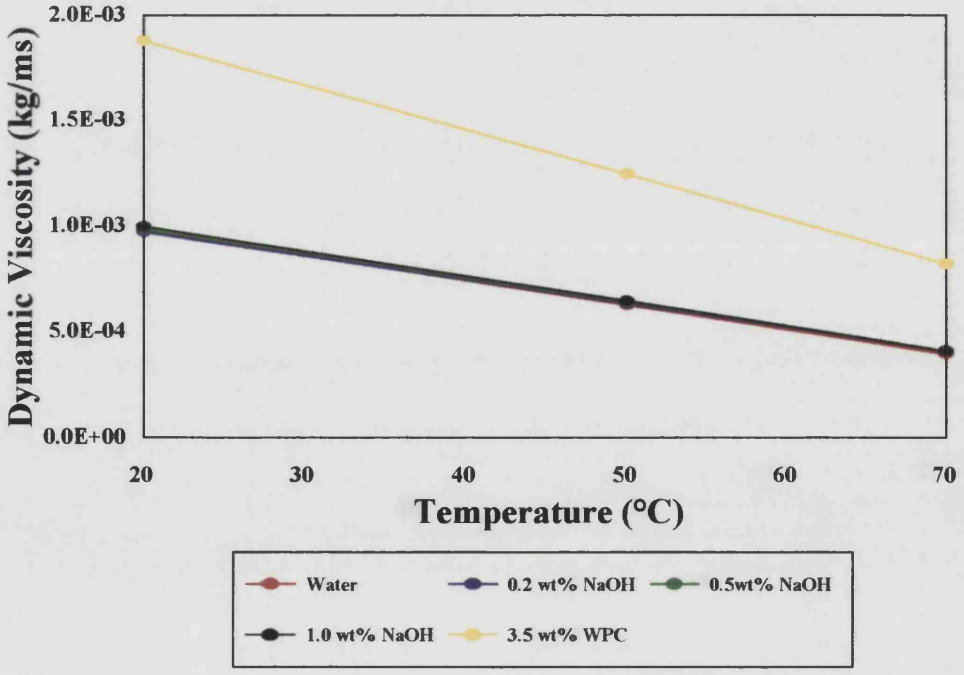



***Figure 3.4b*** *Viscosity variation with temperature for test solutions*

(Figure 3.4a). As expected, viscosity is a strong function of temperature, generally decreasing over the 20 - 70°C temperature range tested (Figure 3.4b).

### *3.1.2.2 Foulant*

The cleaning of membranes fouled with whey proteins constitutes the majority of published data, therefore, the use of a whey protein concentrate (WPC) in fouling experiments presents an industrially relevant choice. Carbelac 35, a free flowing WPC powder, supplied by Carbury Milk Products Ltd was utilised throughout this study. The analytical data and processing conditions of the powdered WPC are detailed in Appendix II. The typical protein composition is given in Chapter 2.

The WPC powder was reconstituted with distilled water to give a 3.5 wt.% protein solution of pH6.4 after 1 hour of mixing.

Figure 3.4a shows a linear decrease in density with increasing temperature for a WPC solution of this concentration. There is a general decrease in viscosity with an increase in temperature for the values examined.

### *3.1.2.3 Cleaning Agents*

Sodium hydroxide was chosen as the principal cleaning agent for this study. Its ability to remove proteinaceous deposits is well documented and it forms the basis of many formulated cleaning agents. Sigma Laboratories Ltd supplied analytical grade sodium hydroxide as easily dissolvable pearls. Figure 3.4a shows the variation in density with increasing concentration for temperatures of 20, 50 and 70°C. An increase in both concentration and temperature caused linear increases in density. For the low concentrations of sodium hydroxide tested ($\leq$ 1.0 wt.%) there was little variation in viscosity at all the temperatures tested. A general decrease in viscosity with an increase in temperature was observed.

Experimental work to test the cleaning ability of nitric acid was carried out using a fuming, 70% v/v solution [Sigma Laboratories Ltd] which was diluted to the required wt.% concentration.

Additional experiments show the effect of proprietary cleaning agents. Ultrasil 11 [Henkel Ecolab Ltd] a formulated membrane cleaning agent based on sodium

hydroxide with the addition of EDTA, surfactants and water was supplied as fine white crystals (Table 3.2).

*Table 3.2 Chemical composition of Ultrasil 11*

| Component | Concentration (wt.%) |
|---|---|
| Sodium Hydroxide | 43.6 |
| EDTA | > 30 |
| Non-ionic Surfactants | < 5 |
| Anionic Surfactants | < 5 |

Micro and Micro 90 [International Products Ltd] are, primarily, laboratory cleaners but have wide applications within industry where they are effective hard surface formulations. The cleaning compounds contain long chain anionic surfactants supplemented by quaternary ammonium salts. Though the detailed composition of each cleaner was unavailable, Micro is known to contain an anti-foaming agent.

## 3.2 ANALYSIS TECHNIQUES

As described in Chapter 2, on-line analysis techniques can determine the functionality of the membrane but cannot ascertain the presence of material which does not affect performance. Off-line visualisation techniques can be used to analyse samples and create a dynamic model. Quantitative, qualitative and mathematical techniques are described which assess how fouling and cleaning processes affect the membrane in terms of permeability, selectivity, cleanability, durability, membrane lifetime, and fouling resistance.

### 3.2.1 Quantitative Analysis

Obtaining a quantitative measure of cleaning efficiency is essential for a critical evaluation of the cleaning process.

### 3.2.1.1 *Permeability*

The measurement of permeate flux ($J$) during cleaning provides kinetic data for evaluation of the cleaning process. The ratio of flux during cleaning ($J_C$) to the water flux ($J_W$), measured under the same conditions of temperature pressure and crossflow velocity, provides a quantitative comparison when membranes are cleaned using different conditions. The percent flux recovery ($\%J_{FR}$) was defined as:

$$\%J_{FR} = \left(\frac{J_C}{J_W}\right) \times 100 \qquad \textbf{(3.1)}$$

Alternatively, cleaning can be described as a reduction of the fouling resistance, $R_F$. At any point during the cleaning process the resistance an be expressed as:

$$R_T = R_F + R_M \qquad \textbf{(3.2)}$$

Where the aim of the cleaning procedure is to reduce $R_F$ to zero such that

$$R_T \approx R_M \qquad \text{at} \qquad t = \infty \qquad \textbf{(3.3)}$$

By considering the rate of change in flux with time (or the rate of change in resistance) the efficiency of different cleaning procedures can be quantified. By determining the changing rates of flux recovery during cleaning, procedures can be optimised so that the correct cleaning agent is applied using the correct conditions at the correct time.

### 3.2.1.2 *Selectivity*

Determination of the individual components present in the permeate gives a quantitative assessment of changes to the selectivity of the membrane.

Chromatographic techniques have been widely used for the rapid analytical separation of whey proteins [Strange *et al* (1992)]. The separation and identification of whey proteins was carried out using an anion exchange column (DEAE MemSep

1000, Millipore UK Ltd) and a method adapted from a Millipore technical note [Millipore (1994)].

High performance liquid chromatography was utilised to quantify the total α-lactalbumin (α-LA), β-lactoglobulin (β-LG) and bovine serum albumin (BSA) in the permeate for both the standard and varied fouling procedures.

Analysis was performed using a Gilson system consisting of two 306 pumps, an 811B mixer and a 115 UV detector. The system was coupled to a SGE LS-3200 auto-sampler/auto injector so that a number of samples could be stored in vials and run with the minimum of operator supervision.

Samples were loaded in 80 mM tris buffer (pH 8.5) and eluted at 3.5 ml/min with a linear NaCl gradient up to 200 mM over 15 minutes. Peaks were analysed by measuring the absorbance at 280 nm. The analysis method was input into the Gilson software as described in the operating manual.

Calibration data for sample component peak height v.'s concentration was obtained by performing serial dilution's of analytical grade BSA, β-LG and α-LA [Sigma Laboratories Ltd] and are given in Figures 3.5a-c.

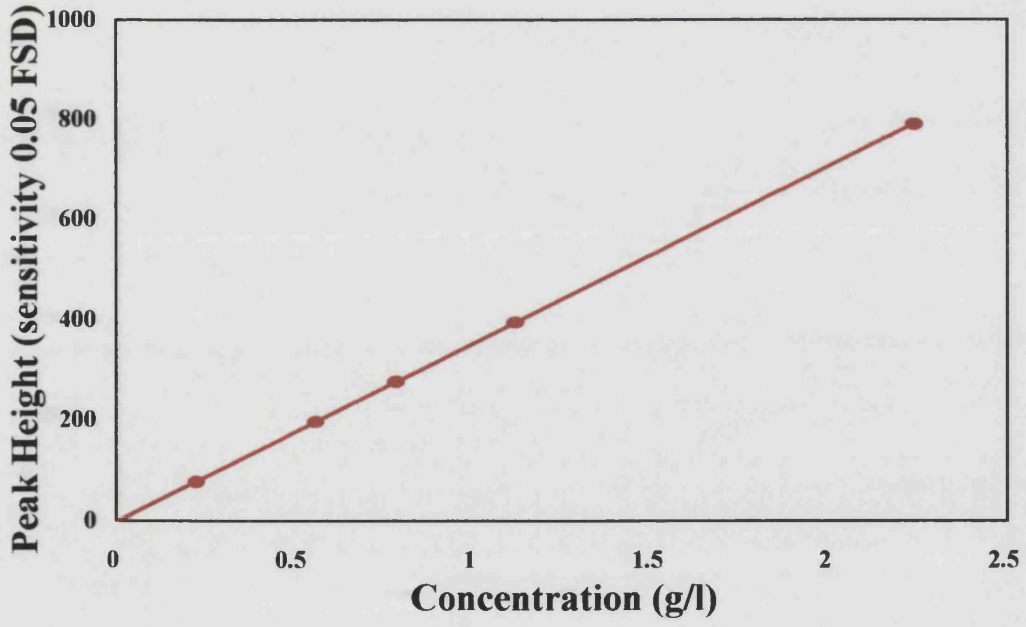



***Figure 3.5a*** *Calibration data for β-LG*

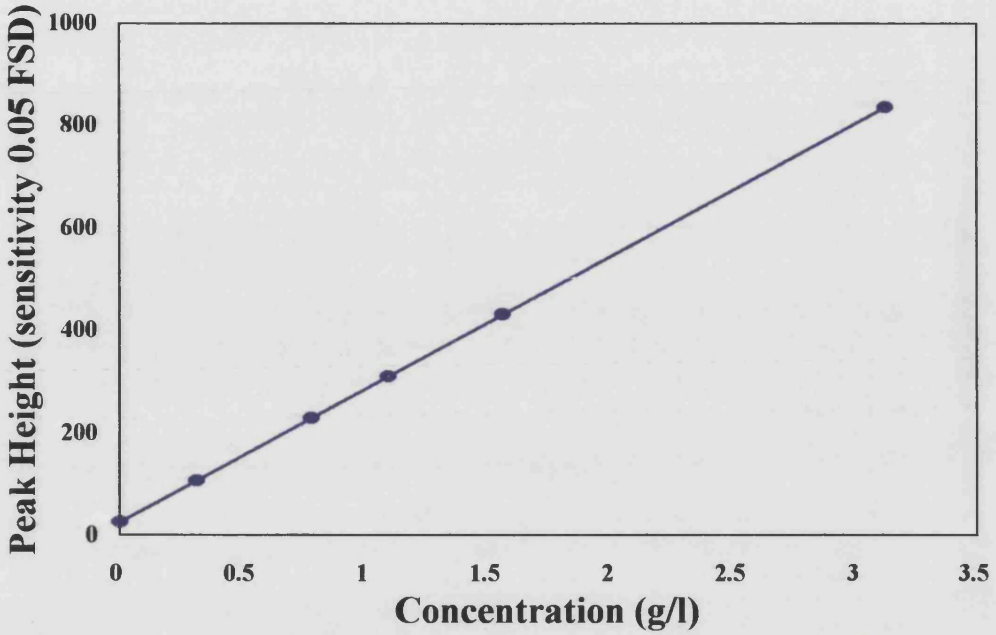



***Figure 3.5b*** *Calibration data for BSA*

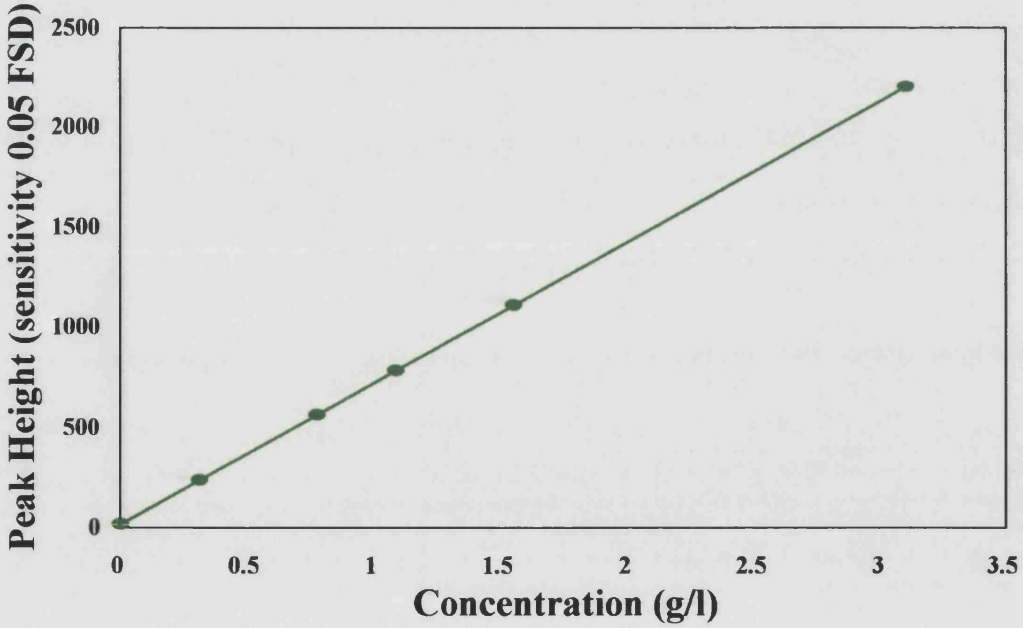



***Figure 3.5c*** *Calibration data for* α-LA

### 3.2.2 Qualitative Analysis

The methods used in this thesis to quantify cleaning efficiency do not characterise the state of the fouled membrane. Qualitative techniques link the membrane functionality with deposit removal, providing valuable information on cleaning mechanisms

#### *3.2.2.1 Visual Examination*

As described in Section 3.3.1 the module was of stainless steel construction. Therefore, the cleaning process could not be observed directly. Inspection of the membrane surface required the module to be dismantled. Visual observations indicated the presence and nature of any gross deposit.

#### *3.2.2.2 Scanning Electron Microscopy (SEM)*

The use of SEM provides a more detailed examination of the state of the membrane surface before, during and after cleaning procedures. Specimens prepared by air or vacuum drying were stuck to SEM stubs with conductive paste. The membrane samples were then sputter coated with a thin layer of gold before viewing with a JSM 6310 Scanning Electron Microscope in combination with an X-ray microanalysis system, LINK AN10000 [Oxford Instruments].

### 3.2.3 Mathematical Analysis

Analysis of the fouling data for each of the membrane systems provides valuable information on the dominant fouling mechanism and consequently, the severity and location of the fouling.

As described in Chapter 2, Field *et al* (1995), have shown that by relating the flux ($J$) to the rate of flux decline ($dJ/dt$), the dominant fouling mechanism i.e. cake, intermediate, standard or complete blocking could be established. This information is important in the selection of the correct cleaning strategy.

Data simulation was carried out using *Micromath Scientist* for Windows Version 2.0 to estimate the unknown parameters through regression analysis.

## 3.3 APPARATUS DESIGN

### 3.3.1 Construction Materials

The materials of construction should not react with the feed solutions to form products which may cause interference. Sodium hydroxide, the primary constituent of most cleaning formulations, is corrosive and can react with many commonly used materials such as aluminium, mild steel, lead, brass, and tin [Coulson and Richardson (1991), Perry (1992)].

Stainless steel, copper, glass and plastics were used for the construction of the experimental equipment. The high tin content of ordinary solder made it unsuitable for use, however, silver solder made a resistant alternative.

### 3.3.2 The Module

A stainless steel membrane module that was designed to house any flat-sheet membrane of 100 x 100 cm, is shown schematically in Figure 3.6. The module was modified to include a double O-ring system to ensure module sealing and to eliminate the effects of lateral flow with non-compressible inorganic membranes. A Vyon™ polymeric insert with pores greater than 100 μm was used to support the membrane test-section

Replaceable perspex inserts allowed channel geometry, and hence crossflow velocity to be controlled. An insert providing 9 channels of 7 mm width, 1 mm height and 86 mm in length was used in this study, unless otherwise stated, to provide a filtration area of 59.85 $cm^2$. Sample calculations of the linear flow rate and Reynolds number for a given volumetric flow rate are given in Appendix III.

TMP was controlled by regulating valves [Swagelok Ltd] and measured using pressure transducers [Druck, ± 0.001 bar] on the feed, retentate and permeate lines.

### 3.3.3 The Cleaning and Fouling Rig

The cleaning and fouling rig, as shown in Figures 3.7a and 3.7b, consisted of calibrated, food grade, holding tanks - a 150 litre cleaning solution tank, a 60 litre feed solution tank and a 250 litre distilled water tank. Process feed solutions were mixed using over-head stirrers designed to standard Rushton turbine geometry [Coulson and Richardson (1991)]. Solutions were used within 30 minutes of preparation.

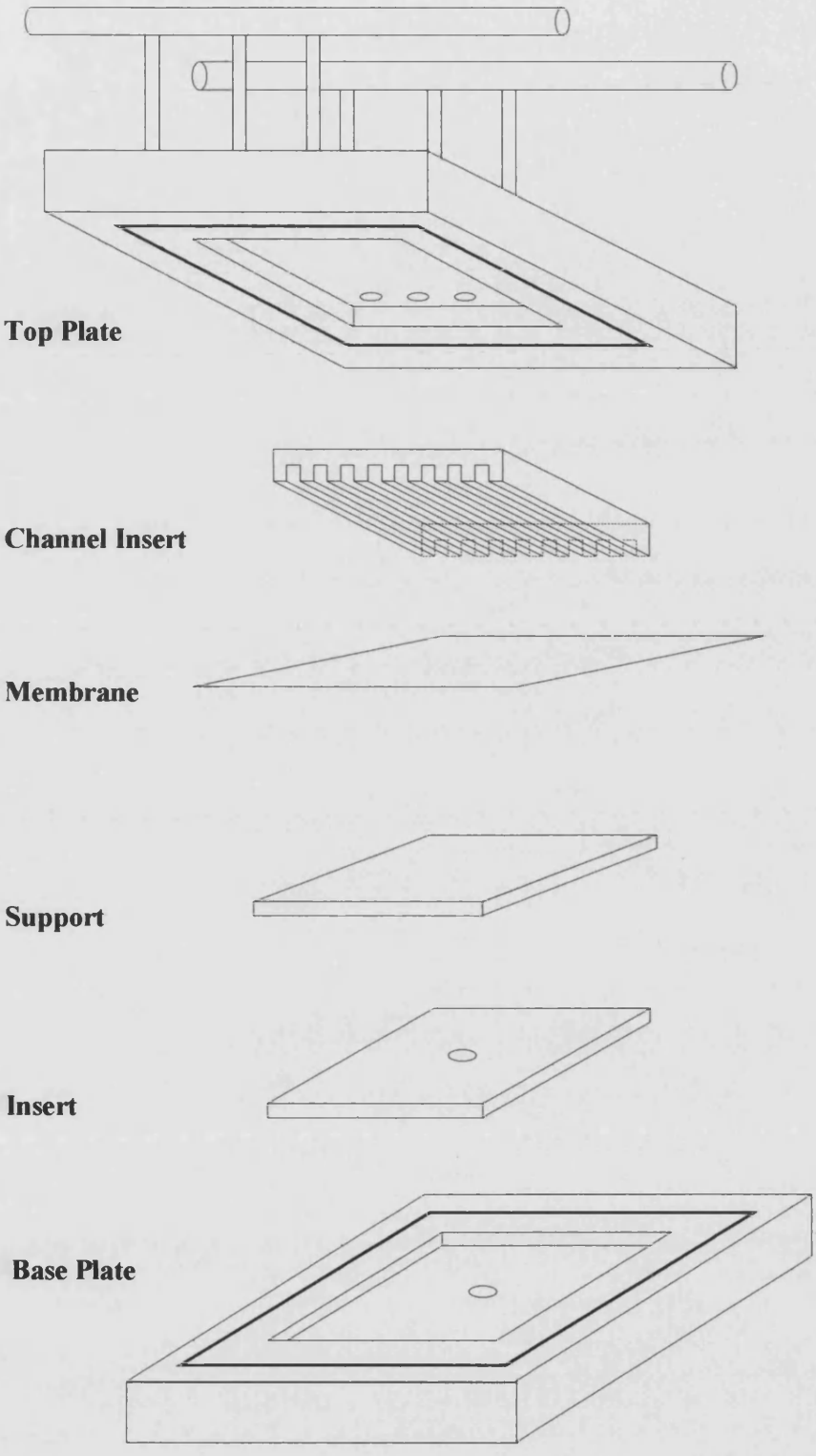



*Figure 3.6* *Schematic diagram of the crossflow module*

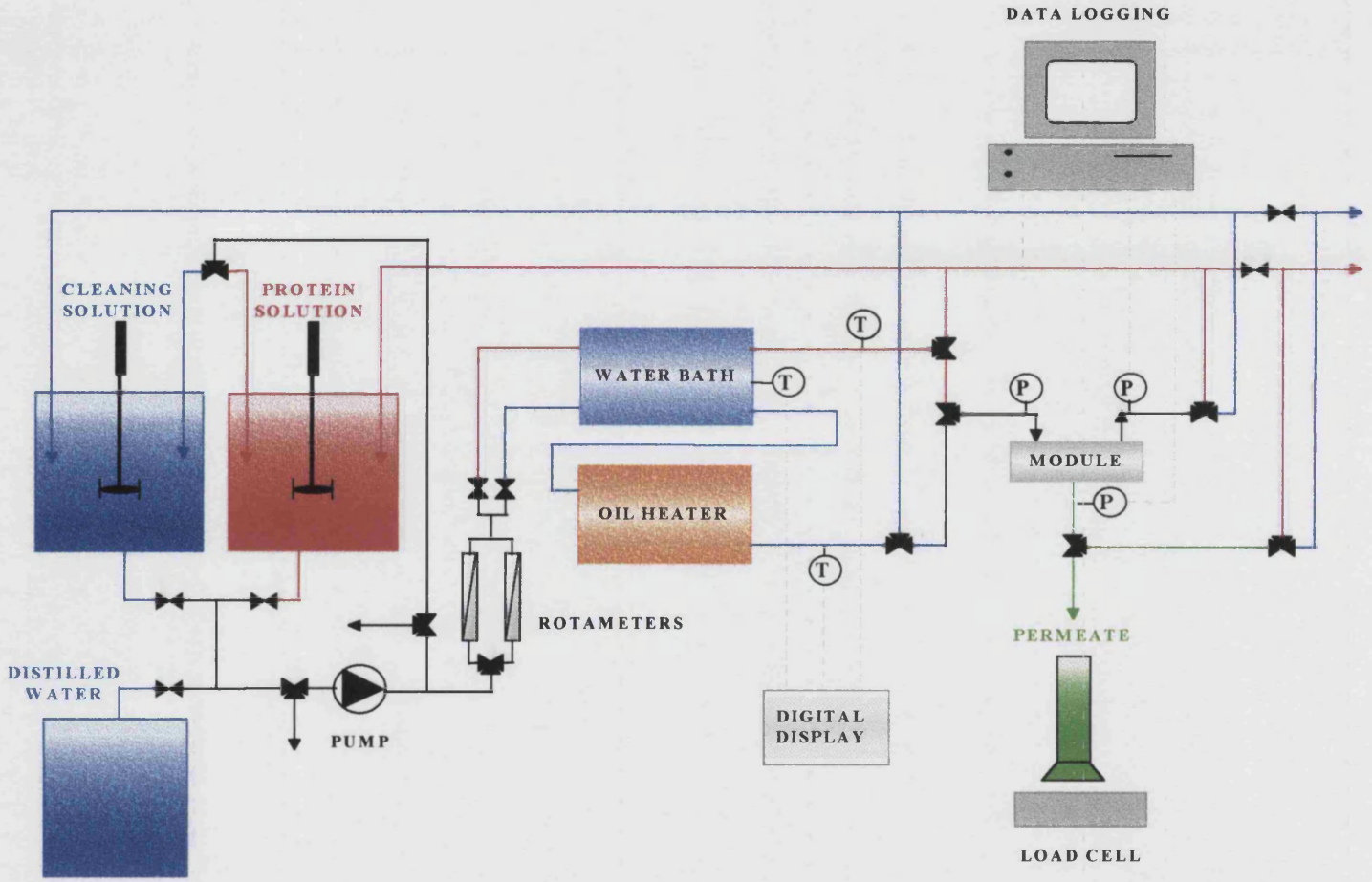



***Figure 3.7a*** *Schematic diagram of the fouling and cleaning rig*

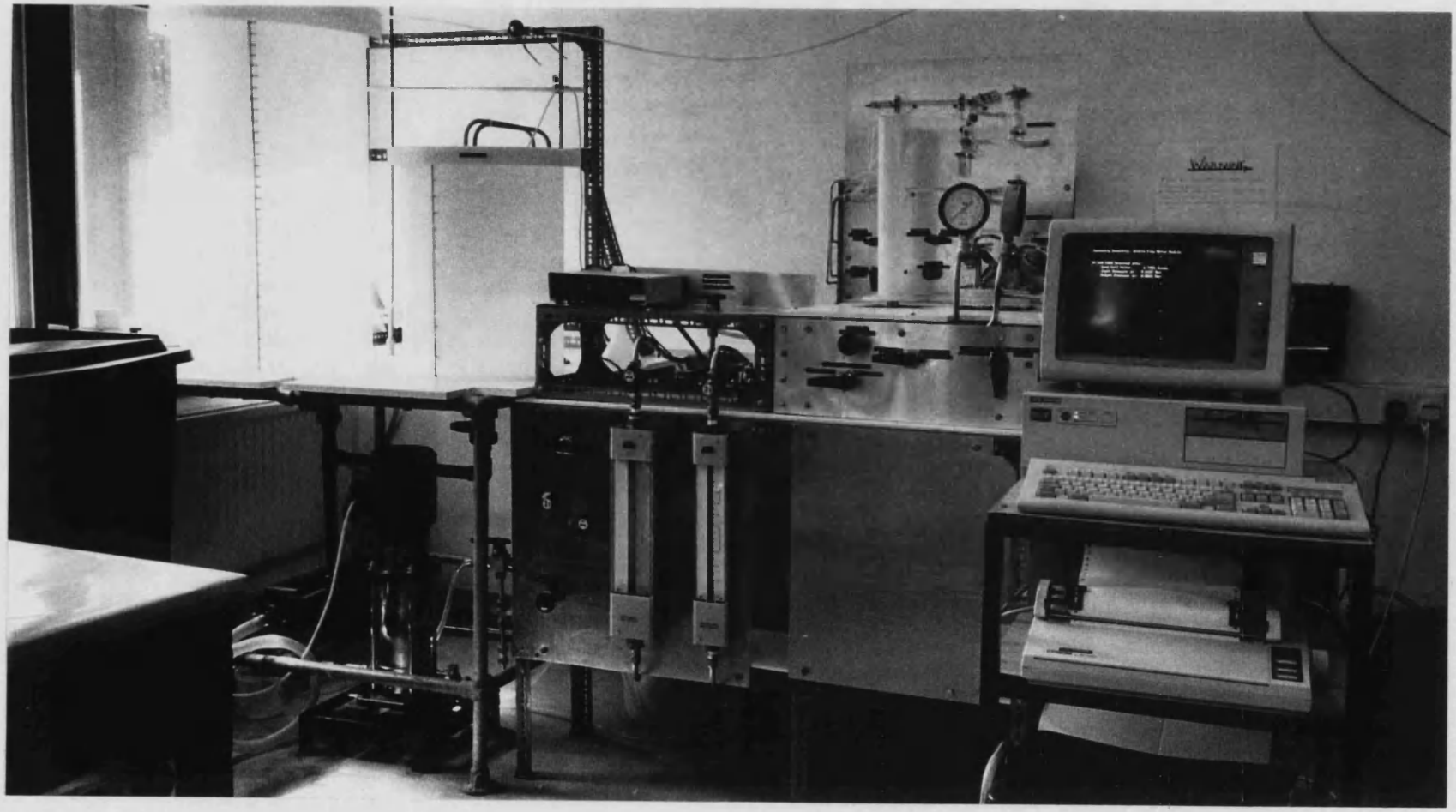


***Figure 3.7b*** *The fouling and cleaning rig*

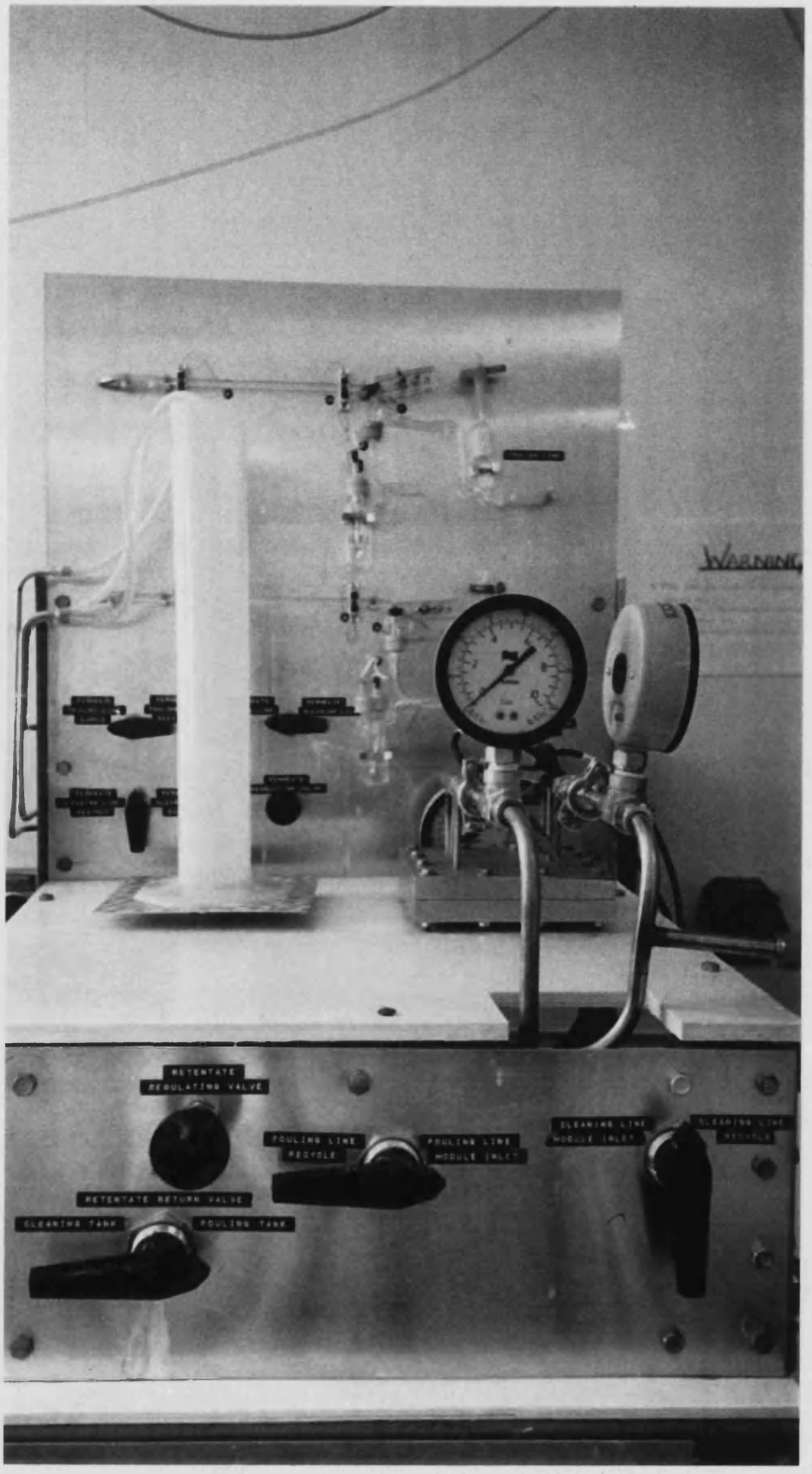



***Figure 3.7c*** *The module set up*

The tanks where connected to a multistage centrifugal pump [Lowara SV208T11M] by 1" diameter, UPVC Durapipe™ tubing and valves.

Process solutions were pumped from the holding tanks, and passed through 30 metres of coiled copper tubing immersed in a 220 litre, thermostat-controlled water bath. The water bath was heated using six 3 kW domestic water heaters and allowed temperature control up to 75°C (± 0.1°C). Additional heating, supplied by a Gallenkamp oil bath [BLC-750 Series], allowed accurate temperature control up to 95°C on the cleaning line. Temperature was measured using platinum thermocouples and a multichannel digital display unit [Digitron].

Circulatory flow rate was controlled, by the use of a by-pass line and a regulating valve [Swagelok Ltd], and measured using calibrated rotameters [KDG Mowbrey Ltd]. The apparatus was capable of processing feed solutions at flow rates of up to 10 $lmin^{-1}$. Each process solution was recycled until the required flow and temperature conditions were attained. Then the flow through the system was redirected to a stainless steel membrane module, as shown in Figure 3.7c.

The process solution was separated by the membrane test section into retentate and permeate streams, using crossflow operation. The retentate stream was recycled to the feed tank, to maintain constant feed concentration. Permeate was collected and measured using a calibrated load cell and stop watch to monitor the flux, or recycled to the feed tank.

The feed lines to the module were constructed of 0.5" o.d 316 stainless steel (i.d 0.372"), as were the return lines. The permeate lines were constructed of 0.25" o.d 316 stainless steel. All connectors and valves supplied [Swagelok Ltd] were of 316 stainless steel, and rated to 10 bar pressure.

Start-up is a critical time. It was important that the feed solution, be it protein solution or cleaning solution, was not diluted or contaminated by the previous process solution. Although the majority of the pipe work for the cleaning and fouling systems was separate, there were some shared lines. To ensure that the feed remained at the desired concentration the solution was run through the complete line and to drain before switching to recycle in order attain the desired flow and temperature conditions for the run. The shutdown of the system required the removal of the process streams. Diluted and neutralised effluent was passed directly to drain.

## 3.4 EXPERIMENTAL PROTOCOLS

### 3.4.1 Membrane Conditioning

New membranes were conditioned by circulating a 50 mM solution of sodium nitrate [Sigma Laboratories LTD] at 50°C with a transmembrane pressure (TMP) of 1.5 bar and a crossflow velocity (CFV) of 1.59 $ms^{-1}$ for 1 hour. This was followed by cleaning the membrane with 0.5 wt.% sodium hydroxide solution for a further hour. Finally the membrane was rinsed for 20 minutes with distilled water using the same conditions.

Prior to membrane fouling the water flux ($J_W$) was recorded at the experimental cleaning conditions. This value was used as a reference for the membrane permeability/cleanliness during each cleaning procedure.

### 3.4.2 Membrane Fouling

As previously discussed, the development of a standard fouling procedure to produce a reproducible and sufficiently severe deposit was essential for the accurate study and appraisal of cleaning kinetics.

In addition, varied fouling conditions were utilised so that the synergistic effect of fouling tendency, location, morphology and permeation characteristics of the deposit could be studied and related to the cleanability of membrane systems.

The rate of flux decline was analysed to ascertain the dominant mechanism of fouling for each membrane system.

#### *3.4.2.1 Standard Membrane Fouling Procedure*

Accurate control of process conditions, during the fouling process, is essential if a reproducible deposit is to be generated for the study of membrane cleaning kinetics.

For each experimental run the 35 wt.% protein powder was reconstituted in distilled water to give 20 litres of solution with a total protein concentration of 3.5 wt.% (pH 6.4). A process temperature of 50°C was chosen to emulate the holding conditions found for the industrial pre-treatment of whey [Luss (1984)]. A moderate TMP of 1 bar and CFV of 1.04 $ms^{-1}$ was utilised during the membrane operation of 1 hour. Both retentate and permeate were recirculated back to the feed tank to maintain a constant feed concentration.

Permeate flux during the microfiltration operation ($J_F$) was monitored to check the progression of the fouling process and to ensure that a reproducible and sufficiently severe deposit was generated.

#### *3.4.2.2 Variable Membrane Fouling Procedures*

Polyethersulphone membrane sections (Supor 100, Gelman Sciences) were fouled using a 3.5 wt.% protein solution. Temperatures of 20, 50 and 70°C were employed to generate deposits during microfiltration runs of 1 hour. TMP's of 0.5, 1.0 and 2.0 bar and crossflow velocities (CFV) of 0.53, 1.04 and 1.59 $ms^{-1}$ were also utilised to produce membrane samples of different fouling tendency, morphology and permeation characteristics. These could then be evaluated for cleanability.

### 3.4.3 Membrane Cleaning

The literature has shown that the chemical cleaning process is complex. To elucidate the mechanisms of membrane cleaning a extensive, systematic, experimental study was required. A programme of cleaning experiments was devised such that the chemical, thermal and hydrodynamic effects could be quantified in terms of membrane functionality. Examination of the membrane test sections before, during and after the cleaning procedures provided valuable information on the mechanisms of deposit removal and hence model design.

#### *3.4.3.1 Formulated Cleaning*

The cleaning efficiency of proprietary cleaning reagents was compared with that of water, 0.2 wt.% sodium hydroxide solution and 0.3 wt.% nitric acid solution [Sigma Laboratories LTD]. The stainless steel, ceramic and PES MF membranes were assessed using the conditions recommended by the cleaning agent manufacturers, as shown in Table 3.3.

#### *3.4.3.2 Sequence Cleaning*

Alkali/acid sequence cleaning was evaluated in terms of the observed flux recovery for the stainless steel and ceramic MF membranes:

Fouled membrane samples were cleaned by recycling a 0.2 wt.% sodium hydroxide solution for 30 minutes at 50°C using a CFV of 1.59 $ms^{-1}$ and a TMP of 0.5 bar. A 10 minute rinse with distilled water was followed by circulating 0.3 wt.% nitric acid solution at 65°C for a further 30 minutes. A final 10 minute rinse with distilled water at 65°C completed the procedure.

Alternatively, the cleaning procedures were reversed. Sintered stainless steel and ceramic membrane samples were cleaned by recycling 0.3 wt.% nitric acid for 30 minutes followed by 10 minutes flushing with distilled water. Further cleaning with 0.2 wt.% sodium hydroxide for 30 minutes was followed by a 10 minute flush with distilled water, under the same conditions completed the acid/alkali sequence.

*Table 3.3 Formulated cleaning agent conditions*

| Cleaning Agent | Concentration (wt.%) | pH | Temperature (°C) |
|---|---|---|---|
| **Distilled Water** | 0 | 5.5 | 50 |
| **NaOH** | 0.2 | 12 | 50 |
| **$HNO_3$** | 0.3 | 1.35 | 65 |
| **Micro** | 2 | 9.6 | 65 |
| **Micro 90** | 2 | 9.2 | 65 |
| **Ultrasil 11** | 0.5 | 11.65 | 50 |

### *3.4.3.3 Caustic Membrane Cleaning*

A systematic matrix of experiments were carried out to evaluate the effects of sodium hydroxide on flux recovery. Each cleaning procedure was carried out for 30 minutes, with full recycle, followed by rinsing with distilled water for a further 30 minutes (no recycle). The permeation rate during cleaning ($J_C$) and rinsing was monitored and used to evaluate the % flux recovery.

The effects of sodium hydroxide cleaning were examined using concentrations between 0 - 1.0 wt.% for the sintered stainless steel, ceramic and PES MF membranes at 50°C with a TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$.

Fouled stainless steel and ceramic membranes were cleaned using a TMP of 0.5 bar with a CFV of 1.59 $ms^{-1}$ and the optimum sodium hydroxide concentration determined for each system for temperatures in the 20 - 70°C range.

The change from laminar to turbulent bulk flow conditions was investigated using cross flow velocities of 0.26 - 1.90 $ms^{-1}$. The flux recovery characteristics were investigated at 50°C using a TMP of 0.5 bar and the optimum sodium hydroxide concentrations, determined experimentally, for the sintered stainless steel and ceramic membranes

Cleaning efficiency was investigated using transmembrane pressures of 0.5 and 1 bar at 50°C with a CFV of 1.59 $ms^{-1}$ for both the inorganic membranes. Additional experiments were carried out which simulated hard surface cleaning by closing the permeate line and utilising a zero TMP differential. Single cleaning runs gave just the final flux recovery value for the 30 minute cleaning period. In order to determine the flux recovery characteristics as a function of time it was necessary to carry out multiple experiments, taking incremental 'snap shots' of the permeability.

#### *3.4.3.4 Visualisation of the Cleaning Process*

Visual examination of the state of the membrane surface before and after cleaning gives an initial indication of the success of each cleaning operation.

Examination of membrane samples using SEM and x-ray microanalysis gave a better indication of the physical state of the surface, such that deposit removal during cleaning could be related to the flux recovery characteristics observed. To investigate deposit removal during cleaning, multiple, incremental experiments were carried out to produce membrane samples where sintered stainless steel membrane were cleaned with 0.2 wt.% NaOH at 50°C with a TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$. In addition, membranes cleaned with 1.0 wt.% NaOH were examined to visualise the physical and morphological changes in deposit structure due to concentration effects.

#### *3.4.3.5 Chemical and Thermal Durability*

The durability of the ceramic and PES membranes was tested against thermal and chemical attack by immersing samples in sealed glass vials and storing them in a thermostatically controlled chamber. Membrane samples were immersed in distilled

water or solutions of 0.5 wt.% NaOH, 2 wt.% NaOH, and 0.3 wt.% $HNO_3$ at 50 and 80°C, for periods of up to 320 hours. Samples were viewed and photographed using SEM techniques to detect any physical damage.

#### *3.4.3.6 Multiple Fouling and Cleaning Cycles*

The effects of standard conditioning, cleaning, fouling and restoration procedures were evaluated through changes in permeability for multiple cycles of use for PES membranes.

#### *3.4.3.7 Fouling and Cleaning Synergy*

The effects of fouling conditions on membrane cleanability were investigated using a systematic protocol to generate deposits with different fouling tendency, morphology and permeation characteristics

A matrix of experiments was employed to investigate temperatures of 20, 50 and 70°C, transmembrane pressures of 0.5, 1.0 and 2.0 bar and crossflow velocities of 0.53, 1.04 and 1.59 $ms^{-1}$ using 3.5 wt.% protein solutions to foul PES MF membranes.

To standardise the results each fouled membrane sample was subsequently cleaned by recycling 0.4 wt.% NaOH at 50°C using a CFV of 1.59 $ms^{-1}$ and TMP of 0.5 bar.

### 3.4.4 Membrane Restoration

In cases where the test cleaning procedure did not restore the water flux to its initial value the membrane was cleaned using the following standard procedure:

A 0.5 wt.% solution of Ultrasil 11 was circulated through the system at 10 $limn^{-1}$ at a temperature of 50°C with the permeate line fully closed for 20 minutes. The system was then flushed with distilled water using the same flow conditions and temperature for 10 minutes. A fresh solution of Ultrasil 11 was then circulated at 10 $lmin^{-1}$ for 20 minutes with the permeate line open, using a temperature of 50°C with a TMP of 1 bar. The system was then flushed with distilled water under the same conditions for a further 10 minutes.

For the polyethersulphone membranes the final cleaning solution contained 100 ppm sodium hypochlorite.

## 3.5 EXPERIMENTAL ERRORS

The objective of the experimental protocols was to minimise errors by controlling process conditions. Biological systems have a significant inherent variability and experimental errors are to be expected, as data will have some degree of scatter. Identification of error sources ultimately improves the results generated.

The errors in this study can be traced to the condition of the membrane, the fouling and cleaning procedures and the analysis techniques used in the assessment of the fouling and cleaning processes.

- **Membrane**

  The initial condition of the membrane was assured by standardising conditioning procedures. Membranes with abnormal permeabilities were discarded.

  Permeability variation during the first three fouling and cleaning cycles made it difficult to assess the stability of the system. Only membranes that had been stabilised were used to generate cleaning data.

  After each fouling and cleaning cycle the membrane was cleaned using the standard restoration procedure to regain an established membrane permeability. The water flux, $J_W$, was taken at the start of each cycle. Again, membranes with abnormal permeabilities were discarded at this stage.

- **Fouling**

  Fouling errors could originate from the condition of the membrane before fouling, changes in foulant composition and the fouling conditions.

  Variations in deposit were minimised by the use of a dried product, obtained in a single batch. WPC was used in preference to raw milk or whey where the quality can be variable due to seasonal and feed changes [Burton (1967)]. The protein solutions were prepared in a cold room at 5°C to prevent microbial contamination. WPC powder was reconstituted in 20 litres of distilled water and mixed for two hours prior to use to ensure hydration of the dried product. The solution was coarse filtered prior to being transferred to the fouling tank.

Fouling conditions were kept as constant as possible, and any membrane that showed significant deviation in permeability during the fouling run was discarded.

Membranes were cleaned within an hour of each fouling procedure.

- **Cleaning**

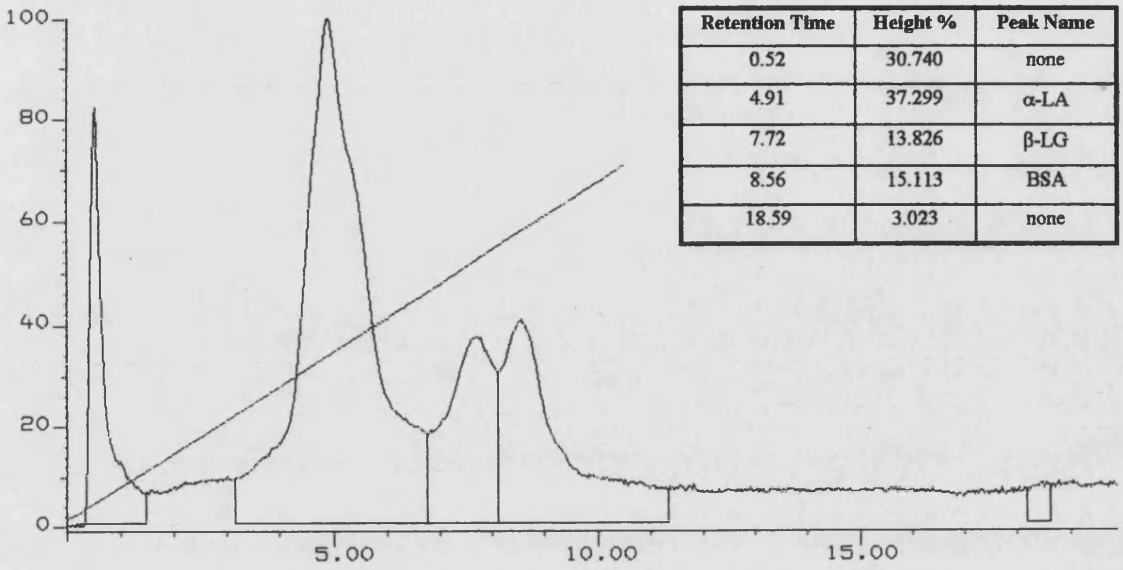
The main source of error is likely to be from variation in cleaning agent composition and the process conditions. The cleaning agents (sodium hydroxide pearls, nitric acid solution, Ultrasil 11, Micro and Micro 90) were purchased in single batches to minimise composition variation. Solutions were prepared 2 hours prior use, ensuring thorough mixing, and the pH of the solution was checked before application.

Solution flowrates were calibrated for each rotameter and thermocouples were tested in ice. Feed, retentate and permeate pressures were measured using identical transducers with a range of 0 - 7 bar and accurately controlled to 2 decimal places

- **Analysis**

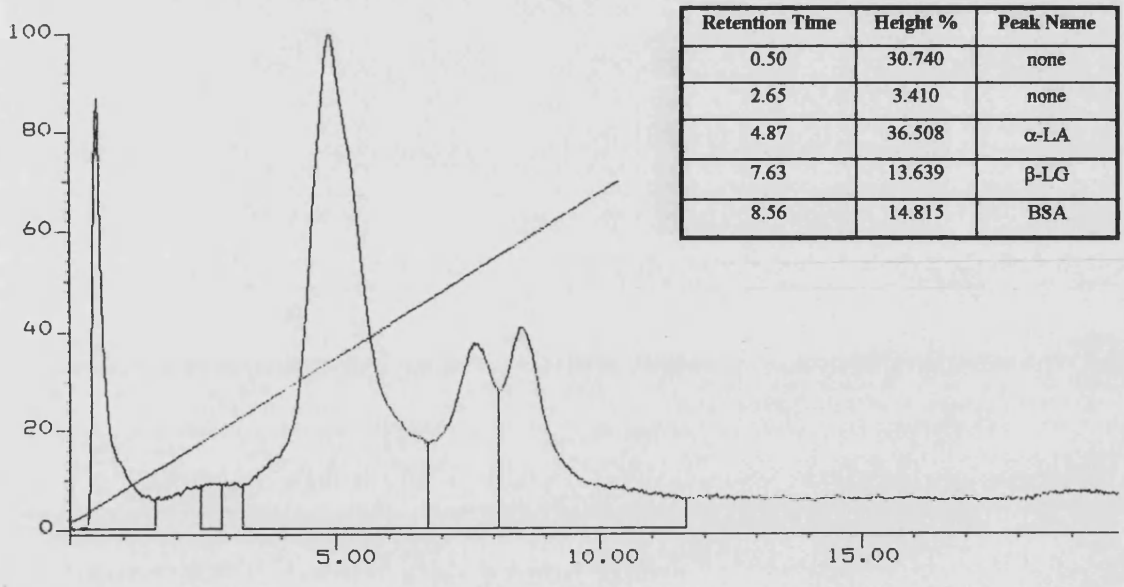
Flux was used as the main criterion for assessing cleaning effectiveness. Flux was measured by incremental weighing of permeate with a load cell. The load cell was calibrated using balance weights for the full range of 0 - 5000 units for up to 1 kg in weight with accuracy of ± 200 mg.

Assessment of the HPLC analysis technique was undertaken by performing duplicate analyses on each test sample. Figures 3.8a and 3.8b show traces for repeated HPLC runs for the identification of whey proteins found in the permeate produced from the membrane processing of a 3.5 wt.% protein solution at 50°C, with a TMP of 1.0 bar and CFV of 1.04 $ms^{-1}$.




| Retention Time | Height % | Peak Name |
|---|---|---|
| 0.52 | 30.740 | none |
| 4.91 | 37.299 | α-LA |
| 7.72 | 13.826 | β-LG |
| 8.56 | 15.113 | BSA |
| 18.59 | 3.023 | none |

***Figure 3.8a*** *HPLC trace for the separation of whey proteins using a MemSep DEAE 1000 anionic exchange column.*




| Retention Time | Height % | Peak Name |
|---|---|---|
| 0.50 | 30.740 | none |
| 2.65 | 3.410 | none |
| 4.87 | 36.508 | α-LA |
| 7.63 | 13.639 | β-LG |
| 8.56 | 14.815 | BSA |

***Figure 3.8b*** *Duplicate HPLC run for the separation of whey proteins using a MemSep DEAE 1000 anionic exchange column.*

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.0 INTRODUCTION

This chapter presents the core experimental work of this thesis. Results are grouped together in terms of the parameter under investigation and described both quantitatively and qualitatively, in terms of performance, resistance to fouling and/or membrane durability.

The generation of a sufficiently severe and reproducible deposit is required for the comparison of cleaning data. Knowledge of the deposit nature, morphology and location is useful in determining cleaning strategies.

Flux recovery is the main criterion for the quantitative evaluation. Kinetic curves are produced to show the changes in flux with time. The influence of cleaning agent type, sequence of application, and the effect of cleaning solution concentration, temperature, crossflow velocity and transmembrane pressure are investigated.

Qualitative analysis by using SEM, x-ray microanalysis and HPLC techniques supplements the quantitative data by linking removal to flux recovery.

The aim of this experimental programme was to elucidate the mechanisms of flux recovery such that the process could be modelled (Chapter 5).

## 4.1 DEPOSIT FORMATION

Figures 4.1a-4.1c show typical fouling curves for the 2 μm sintered stainless steel membrane (Pall Filtration), 0.1 μm ceramic membrane (NWW Acumem Ltd) and Supor 100 PES membrane (Gelman Sciences), used in this study. Each of the membranes was fouled using a WPC powder reconstituted to give a 3.5 wt.% protein solution at 50°C, with a TMP of 1 bar and a CFV of 1.04 $ms^{-1}$.

As expected, the permeation rate for the WPC solution was much lower than the measured water flux. For all the membrane types considered, fouling was rapid. On average, the sintered stainless steel membrane (Figure 4.1a) showed a final flux value of 25 $kg/hm^2$ after a 1 hour filtration run. For the ceramic membrane, the final

value was about 54 kg/hm$^2$. Typically, the PES membranes had final flux values of 45 kg/hm$^2$. In each case, the final flux value represented a decline of over 95%, compared to the given water flux under the same conditions.

Examination of the kinetic data shows that there are three significant periods to the flux decline. A high initial flux rapidly drops off as the protein solution is forced to the membrane surface. The rate of flux decline then steadies off. Finally, there exists a period where the reduced flux remains relatively constant.

Analysis of the characteristic flux profiles was carried out using the modified blocking laws, proposed by Field *et al* (1995), to ascertain the dominant fouling mechanisms. Simulated results for the sintered stainless steel membrane (Figure 4.1a) showed that cake build-up gave the best estimate for the theoretical blocking mechanism, throughout the fouling period. For the ceramic membrane (Figure 4.1b), it was possible to identify the initial and final stages of the flux decline corresponding to the complete blocking of the smallest pores (n=2) and the beginning of cake fouling (n=0). The transition between different fouling stages was gradual, and more complex in the central steps.

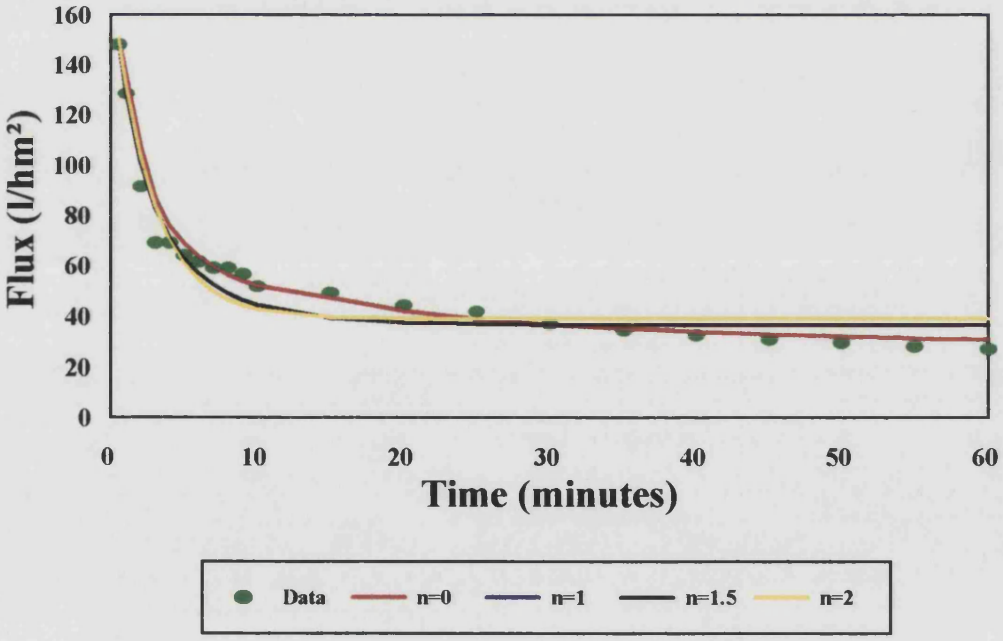



***Figure 4.1a*** *Typical fouling curve for a sintered stainless steel membrane using a 3.5 wt.% protein solution at 50°C, TMP of 1 bar and CFV of 1.04 ms$^{-1}$*

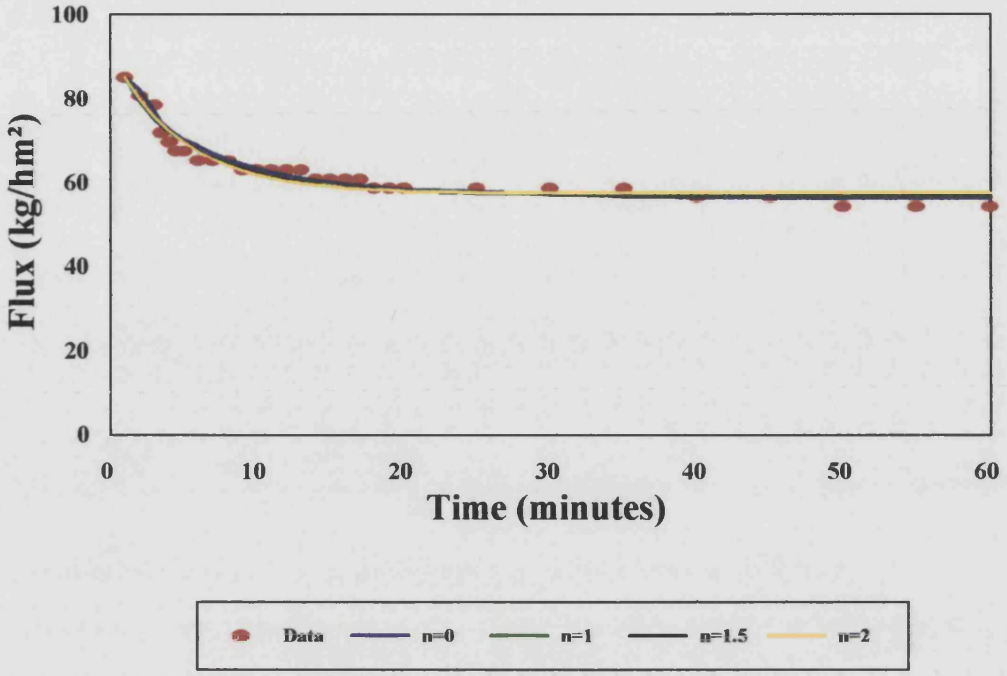



***Figure 4.1b*** *Typical fouling curve for a ceramic membrane using a 3.5 wt.% protein solution at 50°C, TMP of 1 bar and a CFV of 1.04 ms$^{-1}$*

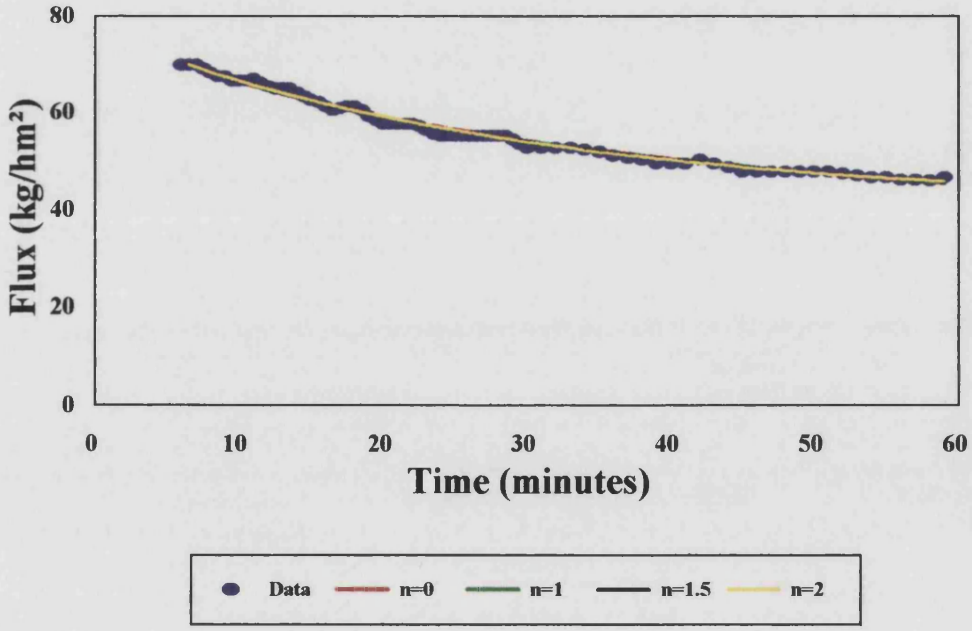
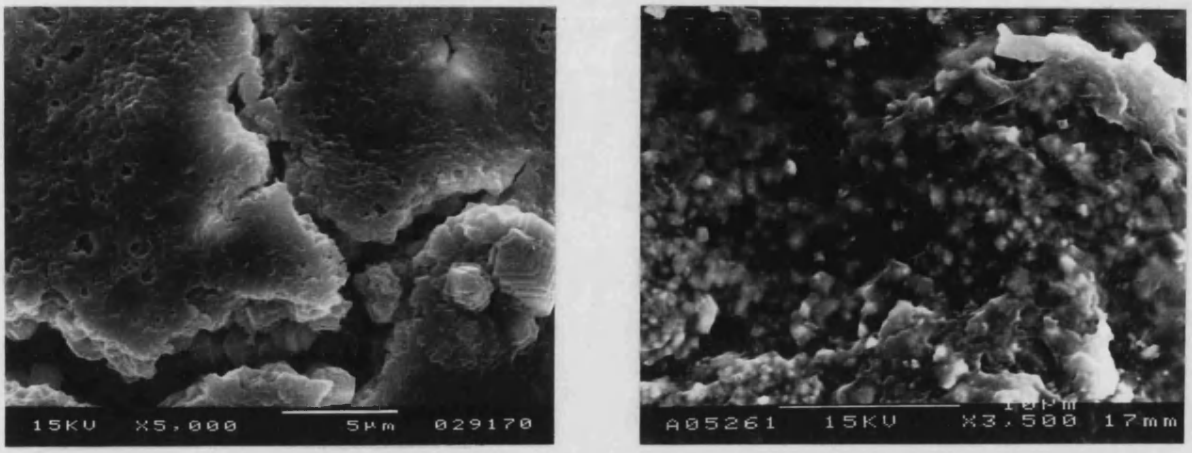



***Figure 4.1c*** *Typical fouling curve for a Supor 100 PES membrane with a 3.5 wt.% protein solution at 50°C, TMP of 1 bar and CFV of 1.04 ms$^{-1}$*

The dominant mechanism for the PES membrane (Figure 4.1c) could not be identified through this analysis of the flux values alone.

SEM's (Figures 4.2a-4.2c), show the typical fouling deposits formed during the standard filtration procedures described above.

**(a)** **(b)**




**(c)**

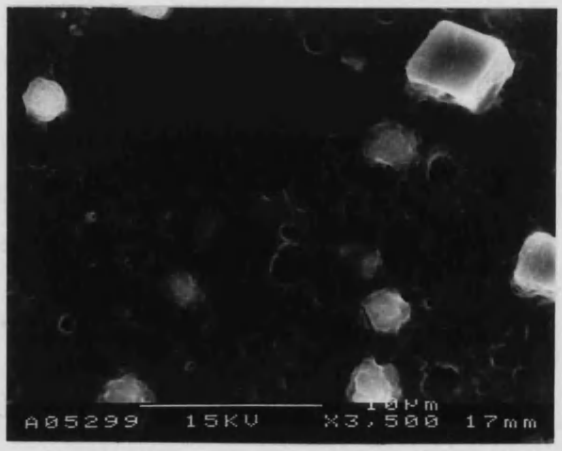
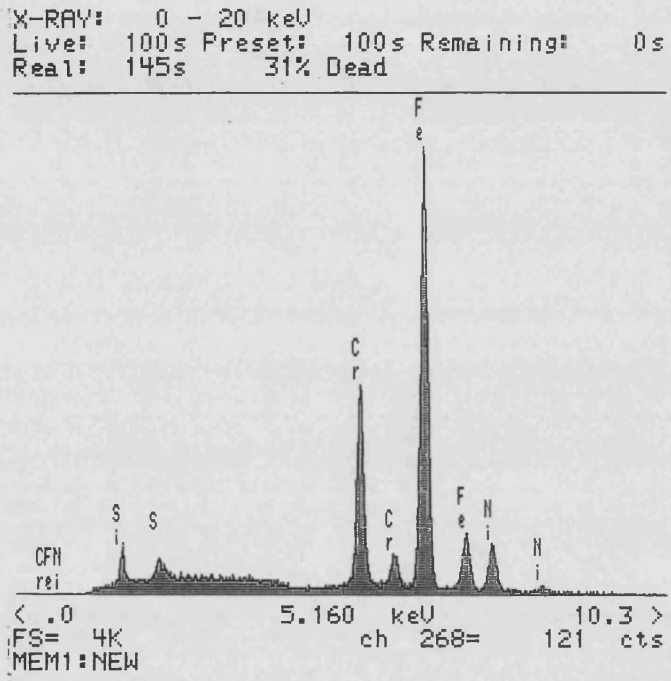



***Figure 4.2*** *Deposit formation using a 3.5 wt.% protein solution at 50°C, with a TMP of 1 bar and a CFV of 1.04 $ms^{-1}$ for 1 hour. (a) sintered stainless steel membrane, (b) ceramic membrane and (c) PES membrane.*

The samples show extensive deposition. Aggregates and minerals are embedded in, and covered by, a matrix of finer material to give 'cake-like' deposits. X-ray microanalysis of the deposits reveals the presence of organic material and high levels of calcium. Nitrogen in the deposit confirms the presence of proteins (Figure 4.3).

**(a)**




**(b)**

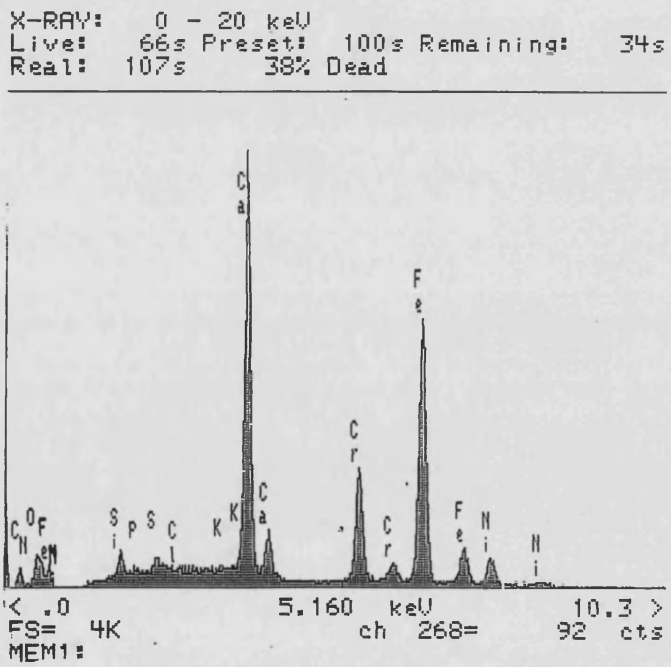



***Figure 4.3*** *X-ray micrographs of stainless steel membrane (a) unused, (b) used.*

While analysis of the deposit has identified the same foulant components, the appearance of the surface deposits differs with each membrane type. As the fouling conditions for each experiment were the same, morphological discrepancies must be due to complex solute-membrane interactions.

The SEM's are consistent with the findings of the fouling analysis. It is thought that material was brought rapidly to the membrane surface of the high flux sintered stainless steel membrane. The high solute concentrations next to the membrane initiated the deposition of large aggregates. Finer grade materials filled in the matrix and formed sheets over the membrane, to give a cake deposit.

Complete blocking of the smaller pores, on the rough surface of the ceramic membrane, is followed by standard or intermediate blocking before cake formation.

With the PES membrane the four phases of deposit formation are super-imposed because of a high porosity and wide pore distribution in these MF membranes.

Analysis of the fouling has defined the state of the membranes and the nature of the deposits. This information is vital for the comparative study and appraisal of cleaning data.

## 4.2 EFFECT OF FORMULATED CLEANING AGENTS

The efficiency of using formulated cleaning agents has been studied in comparison with distilled water, sodium hydroxide and nitric acid. Fouled sintered stainless steel, ceramic and PES membranes were cleaned using the conditions detailed in Table 4.1. The recovery values are represented as a percentage of the clean membrane water flux.

*Table 4.1 Formulated cleaning agent conditions*

| Cleaning Agent | Concentration (wt.%) | pH | Temperature (°C) |
|---|---|---|---|
| **Distilled Water** | 0 | 5.5 | 50 |
| **NaOH** | 0.2 | 12 | 50 |
| **$HNO_3$** | 0.3 | 1.35 | 65 |
| **Micro** | 2 | 9.6 | 65 |
| **Micro 90** | 2 | 9.2 | 65 |
| **Ultrasil 11** | 0.5 | 11.65 | 50 |

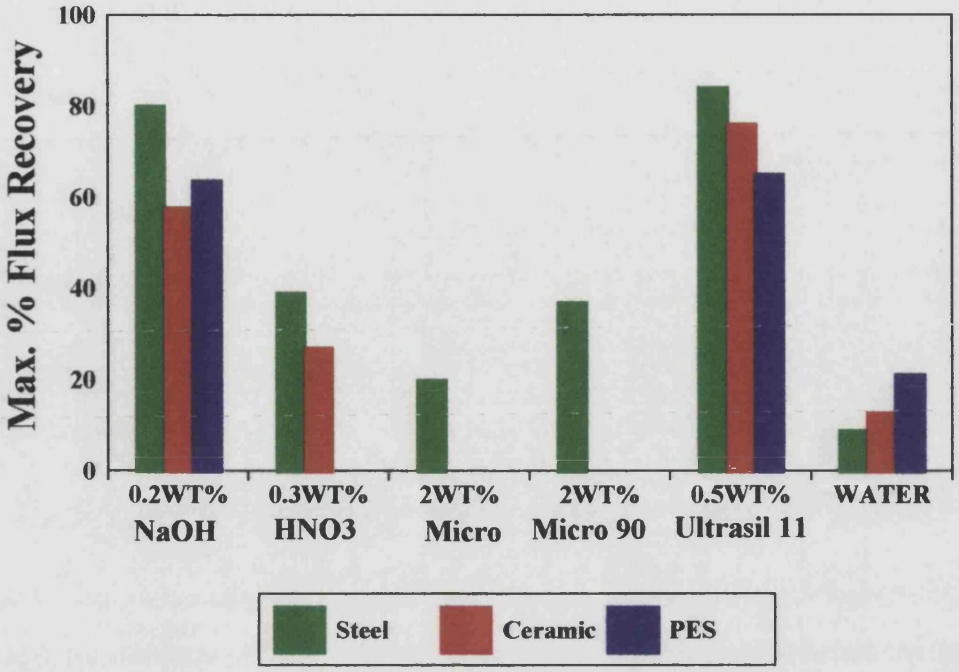



***Figure 4.4a*** *Maximum flux recovery achieved during a 30 minute cleaning run for simple and formulated cleaning compounds*

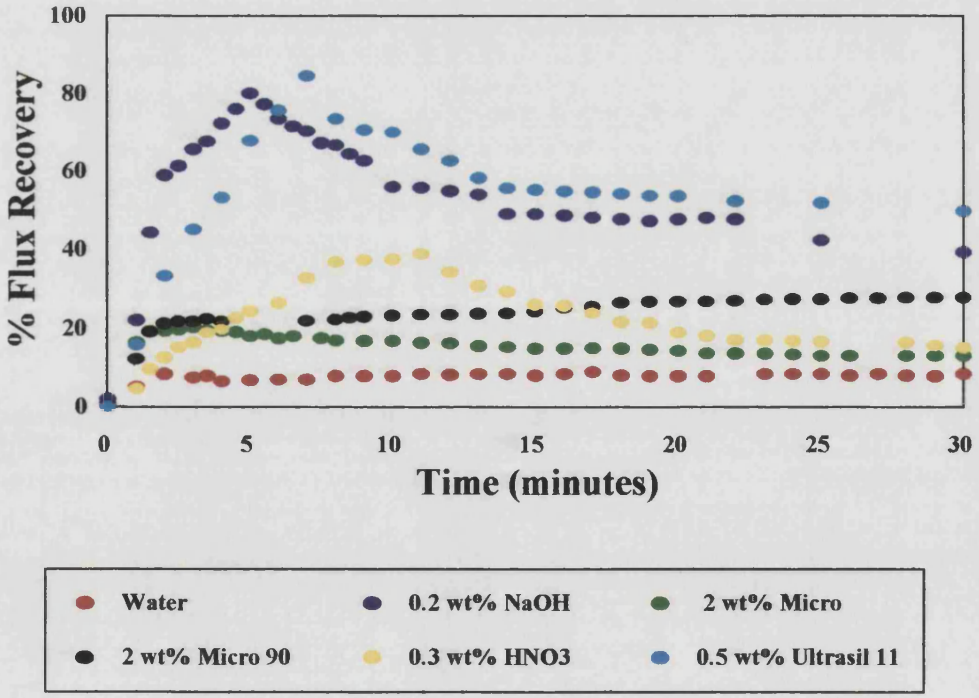



***Figure 4.4b*** *Typical flux recovery curves for the cleaning of sintered stainless steel membranes with simple and formulated cleaning compounds*

Figures 4.4a and 4.4b show the effectiveness of distilled water upon flux recovery at 50°C, using a cross flow velocity of 1.59 $ms^{-1}$ and a TMP of 0.5 bar. Water cleaning recovered just a small fraction of the original water permeability, only 8% for the sintered stainless steel membrane and no more than 22% for the PES membrane. These results indicated that the WPC deposits had low water solubility. The deposits were so tightly bound that removal by fluid mechanical shear alone was not possible.

The addition of sodium hydroxide to water was found to significantly improve flux recovery. Using a caustic concentration of 0.2 wt.%, a maximum flux recovery of 80 % was attained for the sintered stainless steel membranes. 58% of the clean water flux was returned to the ceramic membranes by the same cleaning procedure. After 30 minutes cleaning a flux recovery of about 64% was attained for the PES membrane tested.

Single stage nitric acid cleaning gave poor flux recovery values with both the sintered stainless steel and ceramic membranes tested. Using a concentration of 0.3 wt.% and a moderate temperature of 65°C, resulted in maximum flux recovery values of just 39% and 27% , respectively.

The hard surface-cleaning agent Micro is known to contain anti-foaming agents, and resulted in a poor and unsustainable flux recovery. At the concentration examined Micro 90 gave reduced cleaning efficiency compared to sodium hydroxide and Ultrasil 11, but the flux recovery achieved was sustained. However, the cleaning agent had poor rinsing qualities.

Ultrasil 11, is a caustic based cleaning compound with the addition of EDTA and surfactants. A recommended cleaning concentration of 0.5 wt.% gave the highest flux recovery values of all the cleaning procedures tested. Cleaning restored 65% of the flux for the PES membrane, 76% for the ceramic membrane and 84% for the sintered stainless steel membrane.

High flux recovery values found experimentally for caustic based cleaning agents, and the comparatively low values for cleaning with nitric acid, suggest that the deposit is predominantly organic, not mineral. Examination of the cleaning profiles for the sintered stainless steel membrane (Figure 4.4b), showed a sharp flux recovery during the first few minutes with caustic based cleaning compounds. This can be explained by the removal of proteinaceous deposits, easily solubilised by sodium

hydroxide. The 'sheet like deposit observed on the SEM's, has been described by several researchers [Lee and Merson (1975), Nisbet *et al* (1981), Vetier *et al* (1988), Gésan *et al* (1993)] as the whey protein β-lactoglobulin.

EDTA is used to solubilise minerals and prevent redeposition of removed foulants. Ultrasil 11 improved cleaning ability by as much as 18% for the ceramic membrane, compared to the performance of 0.2 wt.% NaOH. The results indicate that the solubility of minerals plays an important role in the flux recovery process. Surfactants increase the contact between cleaning agent and the foulant, promoting reaction and removal. Surfactant based compounds, such as Micro 90, may prove more suitable agents at lower concentrations. The detrimental effect of anti-foaming agents has been described previously by Yamagiwa *et al* (1993), who showed that these compounds could permanently reduce the capacity of MF membranes, which is consistent with the findings here.

## 4.3 EFFECT OF CLEANING AGENT SEQUENCE

Sintered stainless steel and ceramic membrane systems were cleaned with solutions of 0.3 wt.% nitric acid at 65°C and 0.2 wt.% sodium hydroxide at 50°C, in sequence. A CFV of 1.59 $ms^{-1}$ and a TMP of 0.5 bar was employed throughout the cleaning procedures.

Cleaning the sintered stainless steel membrane with 0.2 wt.% sodium hydroxide during the first stage (Figure 4.5a), resulted in a maximum flux recovery of 80% after 5 minutes, which declined to 44% during the next 25 minutes of cleaning.. A further operation with 0.3 wt.% nitric acid gave the total procedure a maximum flux recovery of 55%. When applied in reverse order, nitric acid cleaning resulted in a maximum flux recovery of 39%, before declining to a terminal value of 16% after 30 minutes cleaning. The following alkali cleaning stage resulted in a maximum recovery of 71%.

For the ceramic membrane, first stage cleaning with 0.3 wt.% nitric acid resulted in a low but sustainable flux recovery (27%), with little further flux recovery during the rinsing phase (Figure 4.5b). The following alkali cleaning procedure with 0.2 wt.% sodium hydroxide resulted in a final flux recovery of 60%. It is worth noting that the flux recovery did increase to 80% during the final rinse.

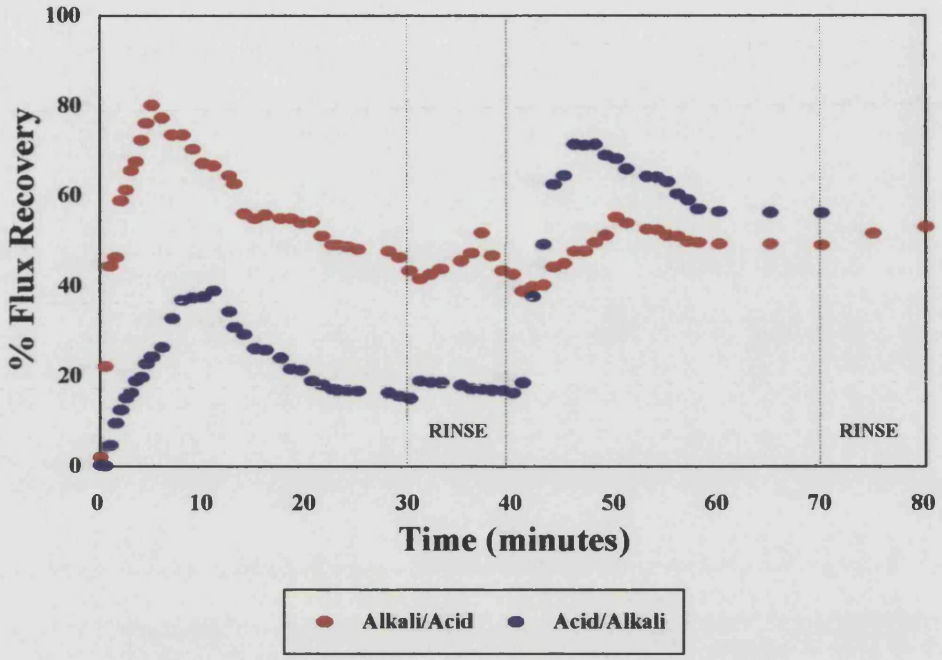



***Figure 4.5a*** *Typical flux recovery curves for alkali/acid sequence cleaning using a sintered stainless steel membrane with a CFV of 1.59 $ms^{-1}$ and TMP of 0.5 bar.*

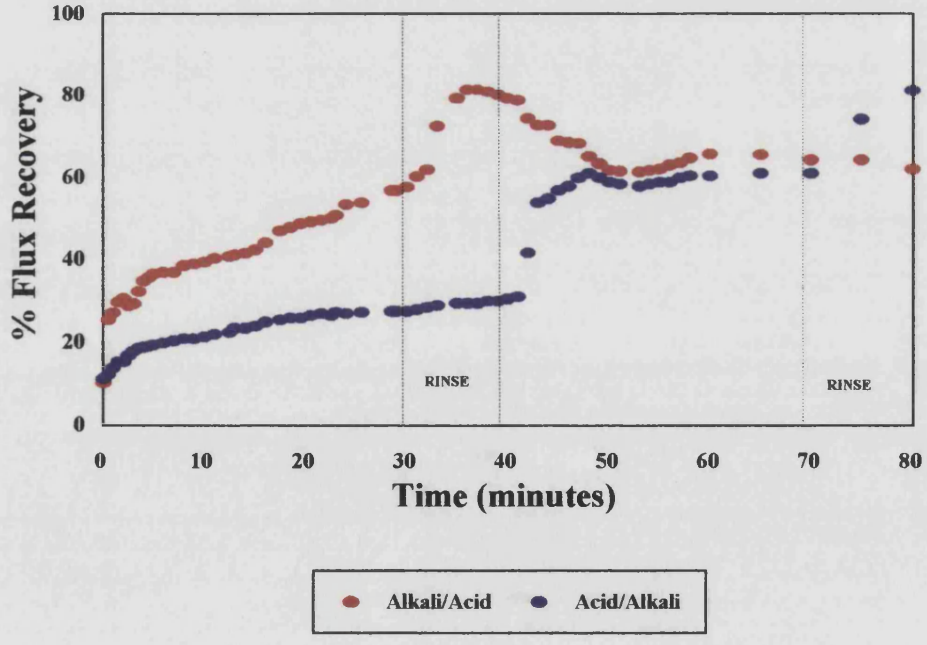



***Figure 4.5b*** *Typical flux recovery curves for alkali/acid sequence cleaning using a ceramic membrane with a CFV 1.59 $ms^{-1}$ and TMP of 0.5 bar.*

First stage cleaning with 0.2 wt.% sodium hydroxide resulted in an initial flux recovery of 58%. A further operation with 0.3 wt.% nitric acid gave a final flux recovery of 64% after 70 minutes of the cleaning procedure.

The maximum flux recovery was less for the two-stage cleaning regimes than for the single stage sodium hydroxide cleaning performance. The poor flux recovery values sustained during cleaning with nitric acid can be explained by the nature of the deposit. Nitric acid reacts with the protein, decreasing its solubility and increasing the tenacity of the deposit, making it more difficult to remove. Surface protein reduces the acids ability to penetrate the cake and remove any mineral deposits.

## 4.4 EFFECT OF SODIUM HYDROXIDE CLEANING

### 4.4.1 Concentration

Figure 4.6a shows the maximum % flux recovery values achieved for sintered stainless steel membranes, using the standard cleaning conditions of 50°C, CFV of 1.59 $ms^{-1}$ and a TMP of 0.5 bar, during cleaning runs of 30 minutes.

As described previously, using water to clean the fouled membrane results in only a small flux recovery, amounting to no more than 8% of the initial water flux. The addition of sodium hydroxide was found to significantly improve recovery. The use of a 0.05 wt.% sodium hydroxide solution increased the maximum % flux recovery three-fold. As the sodium hydroxide concentration was increased, so the flux increased dramatically. A sodium hydroxide concentration of 0.2 wt.% resulted in an optimum flux recovery value of 80%. Further increases in sodium hydroxide concentration did not aid the flux recovery process, but resulted in lower flux recovery values. The use of 1.0 wt.% gave approximately the same maximum flux recovery value as when 0.05 wt.% was used. Sodium hydroxide was unable to fully restore permeability under any of the conditions tested.

The time taken to reach the maximum flux recovery shows a steep decline from 25 minutes when water is used to clean the membrane, to 6 minutes when 0.1 wt.% sodium hydroxide is employed (Figure 4.6b). The maximum flux recovery increases from 8% to 67% for the same concentration range. The effect of increasing the concentration, from 0.1 - 0.8 wt.%, upon the time to reach the point of maximum flux recovery was a steady drop from 6 minutes to 1 minute.

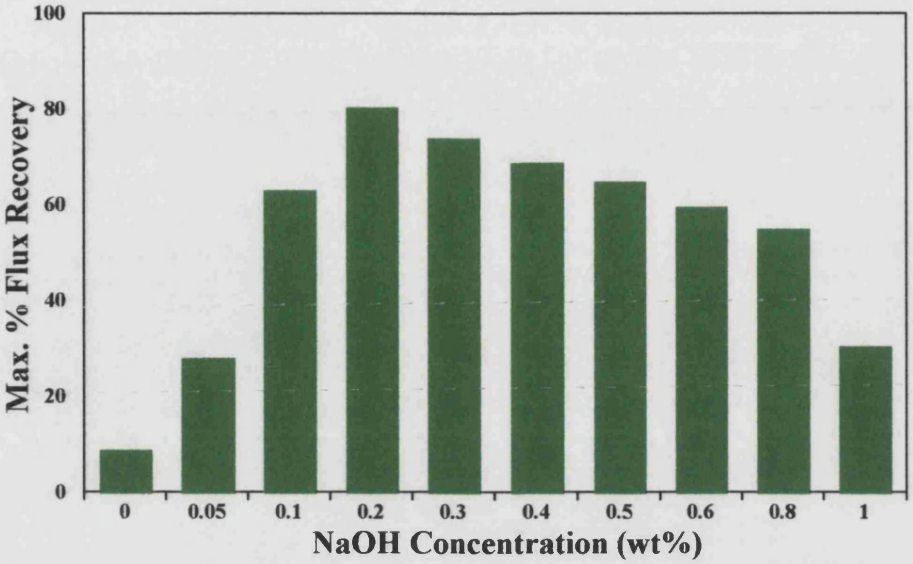



***Figure 4.6a*** *Effect of sodium hydroxide concentration on maximum % flux recovery for a sintered stainless steel membrane at 50°C, TMP 0.5 bar, CFV 1.59 $ms^{-1}$*

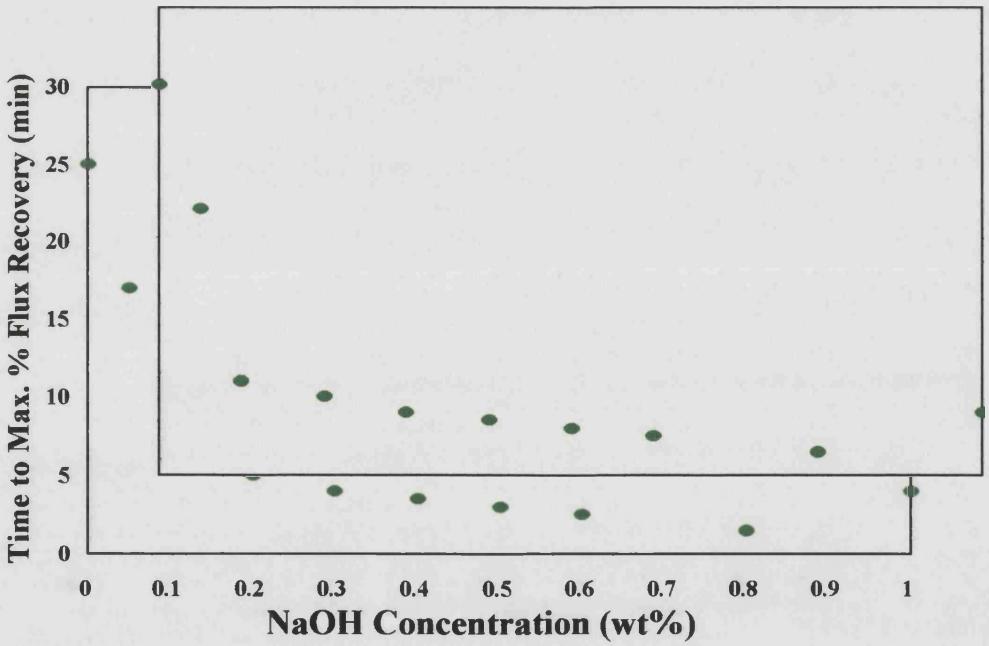



***Figure 4.6b*** *Effect of sodium hydroxide concentration on the time to reach the maximum % flux recovery for sintered stainless steel membrane at 50°C, TMP 0.5 bar, and CFV 1.59 $ms^{-1}$*

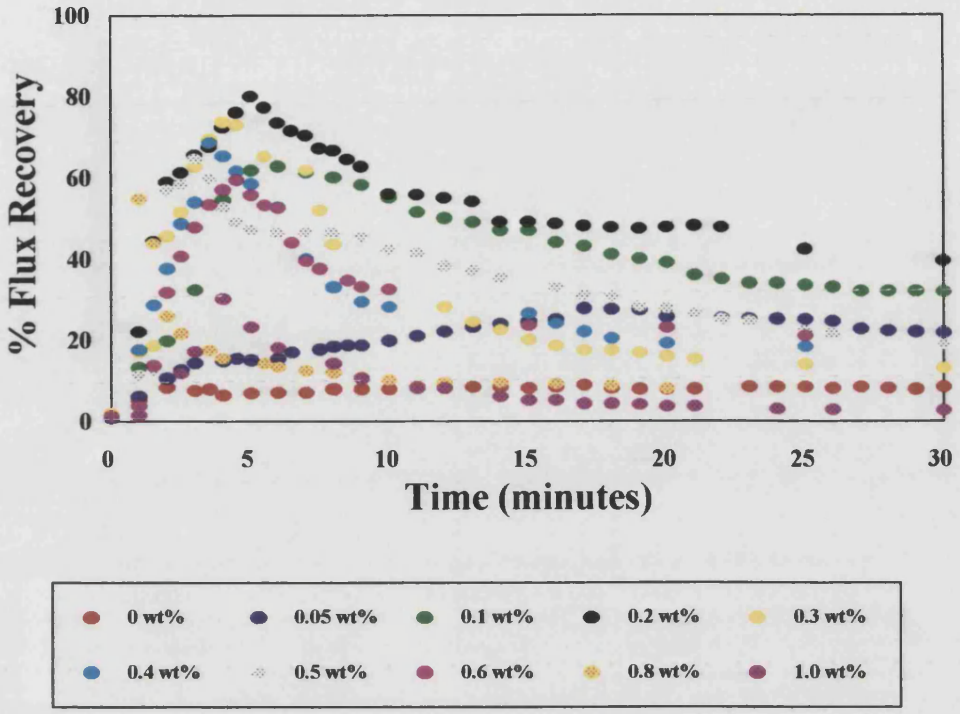



***Figure 4.6c*** *Typical flux recovery curves for a sintered stainless steel membrane using sodium hydroxide at 50°C, TMP 0.5 bar, CFV 1.59 ms$^{-1}$*

Typical flux recovery profiles obtained during cleaning (Figure 4.6c), show that low flux values are quickly increased to a maximum, before decaying back towards a terminal flux value. Visualisation of the cleaning process, using a NaOH concentration of 0.2 wt.% (Section 4.5), showed that gross proteinaceous deposits were removed from the surface of the membrane very quickly. After 6 minutes cleaning, only mineral deposits could be seen on the membrane surface. However, x-ray micrographs of the membrane at this time, revealed the presence of organic material, which may have been in the pores of the membrane. The flux decline observed after reaching the peak flux recovery, may be due to the presence of this in-pore material.

A 0.1 μm ceramic membrane was used to study the flux recovery characteristics for sodium hydroxide cleaning, with concentrations of 0 - 1.0 wt.%, at 50°C, using a CFV of 1.59 ms$^{-1}$ and a TMP of 0.5 bar. Results are presented as a plot of the maximum % flux recovery against concentration (Figure 4.7a) and as an overlay plot of the % flux recovery against time (Figure 4.7b).

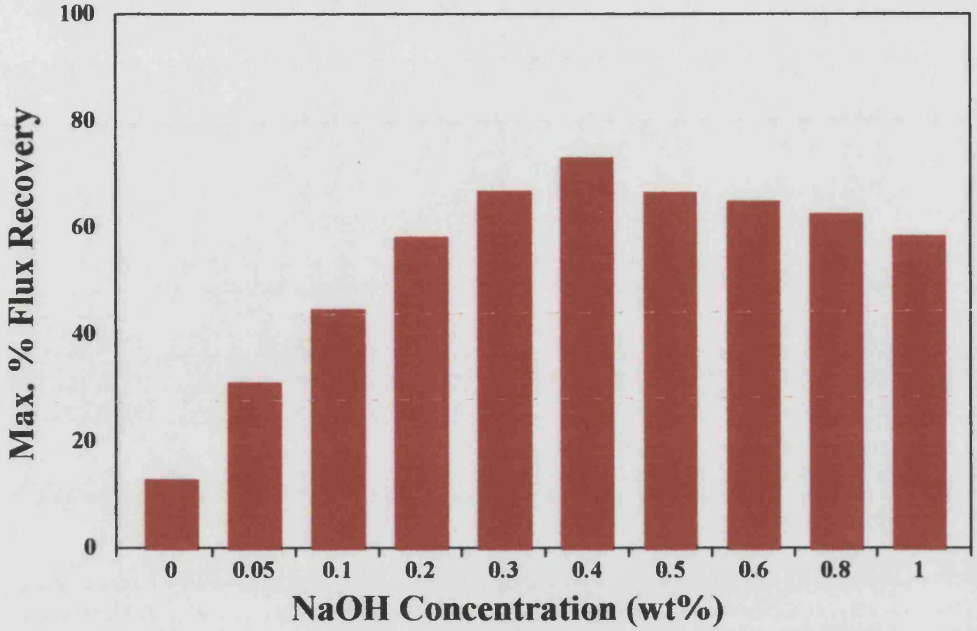



***Figure 4.7a*** *Effect of sodium hydroxide concentration on maximum % flux recovery for a ceramic membrane at 50°C, TMP 0.5 bar, CFV 1.59 $ms^{-1}$*

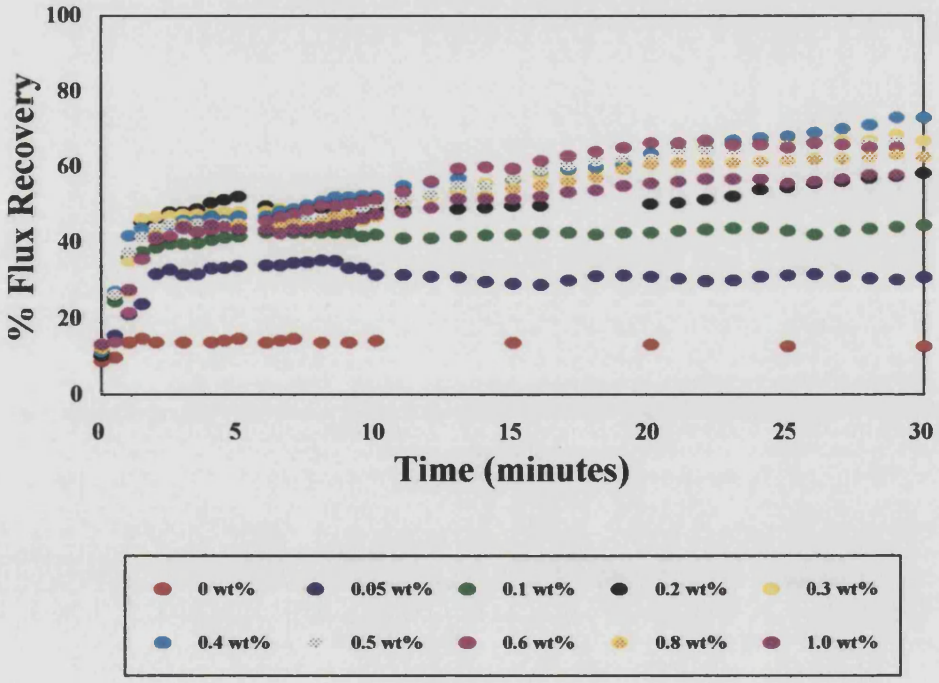



***Figure 4.7b*** *Typical flux recovery curves for a ceramic membrane using sodium hydroxide at 50°C, TMP 0.5 bar, CFV 1.59 $ms^{-1}$.*

As established in the previous section, flux recovery in the absence of a cleaning agent was poor. Water cleaning resulted in a maximum flux recovery of just 12%, after 30 minutes (Figure 4.7a). The addition of sodium hydroxide to the system gave considerably higher flux recovery values. Using a 0.05 wt.% sodium hydroxide solution increased the flux recovery by a factor of 2.5, to give a maximum flux recovery of 31%. For the ceramic membrane, an optimum concentration of 0.4 wt.% gave the highest flux recovery of 73%.

Figure 4.7b shows the typical cleaning curves generated during sodium hydroxide cleaning. The overlay plot shows that the rates of flux recovery during the first 2 minutes were very similar for all the sodium hydroxide concentrations above 0.05 wt.%. This sharp increase in flux recovery, within the first 2 minutes of contact with the caustic cleaning solutions, was followed by 28 minutes of gradual flux increase. However, during this second phase, increases in the sodium hydroxide concentration, up to 0.4 wt.%, brought a corresponding increase in the flux recovery rate. Using sodium hydroxide concentrations above this value reduced the rate, resulting in lower final flux values.

Experiments were carried out for concentrations of 0.1 - 1.0 wt.% sodium hydroxide to determine the flux recovery characteristics of fouled Supor 100 PES MF membranes. As with the previous studies, a temperature of 50°C, a CFV of 1.59 $ms^{-1}$ and a TMP of 0.5 bar were employed.

Figure 4.8a shows a graph of maximum % flux recovery plotted against concentration. Again, poor flux recovery was found using water to clean the PES membrane, though a flux recovery of 22% was considerably higher than what was achieved with the inorganic membranes. The use of 0.1 wt.% NaOH increased the flux recovery by 15%. There was little difference found in the cleaning response for concentrations between 0.2 wt.% and 0.5 wt.%. These cleaning procedures achieved approximately the same overall flux recovery of 63%. There was a decline in the final flux recovery achieved for concentrations above 0.5 wt.%. Employing a 1.0 wt.% sodium hydroxide solution gave a maximum flux recovery of only 46%, achieving just 73% of the optimum flux recovery value.

Examination of the kinetic data (Figure 4.8b) showed that the flux recovery rate increased when low concentrations of sodium hydroxide were used to clean fouled PES

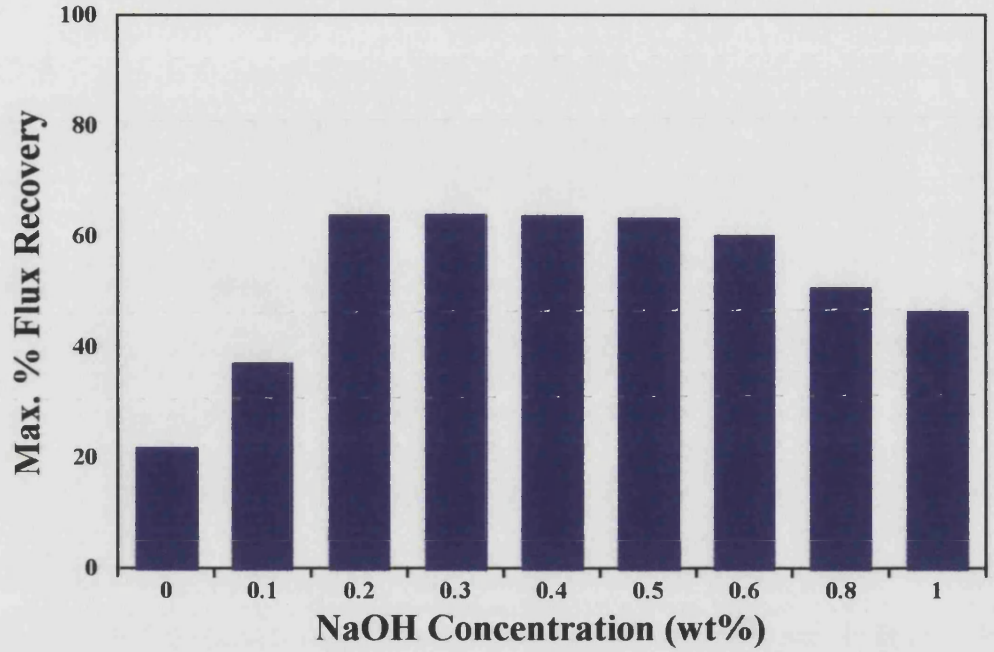



***Figure 4.8a*** *Effect of sodium hydroxide concentration on maximum % flux recovery for a Supor 100 PES membrane at 50°C, TMP 0.5 bar, CFV 1.59 $ms^{-1}$*

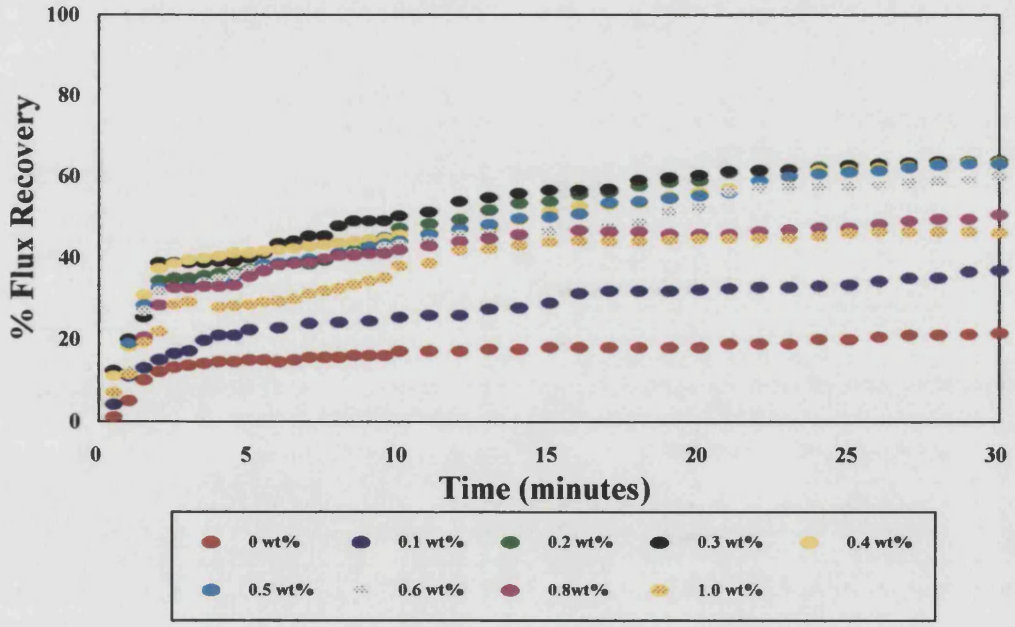



***Figure 4.8b*** *Typical flux recovery curves for a Supor !00 PES membrane using sodium hydroxide at 50°C with TMP 0.5 bar, CFV 1.59 $ms^{-1}$*

membrane samples. For sodium hydroxide concentrations of 0.2 - 0.5 wt.% the flux recovery profiles were synchronous. A sharp flux recovery, during the first 2 minutes cleaning, recovered about 40% of the original water flux. The cleaning rate then decreased, as just 10% of the available flux was recovered within the next eight minutes or so. The flux recovery over the next 20 minutes was gradual and slow.

For the three membrane systems studied, the small increase in flux with water represents the removal of loosely bound material from the deposit matrix. As described previously, deposit formation is a strong function of the solute-membrane interaction. The increased recovery observed during the rinsing of the PES membrane suggests that the surface deposits are less tenacious with this membrane, than those found with the inorganic membranes.

Low levels of sodium hydroxide improve cleaning, increasing the rate of flux recovery and the maximum % flux recovery achieved. Optimum cleaning concentrations of 0.2 and 0.4 wt.% have been identified for the sintered stainless steel and ceramic membranes, respectively. Utilising concentrations in the 0.2 -0.5 wt.% range resulted in the best cleaning performance for PES MF membranes. Increases in the sodium hydroxide above these optimum values did not aid the cleaning process, but resulted in lower maximum flux recovery values.

The existence of cleaning agent optima has been reported for caustic cleaning agents, for both membrane systems and hard surfaces (Section 2.3.3.2). The biochemistry of proteins at very high pH levels is an area which has received little scientific investigation. To explain the optimum cleaning agent concentrations found for the removal of WPC and milk deposits from hard surfaces, Bird (1993) proposed that increased chemical concentrations induced chemical changes, which were more important than fluid mechanical effects. His observations of WPC deposits, showed that the deposit underwent morphological changes which were concentration dependent, when contacted with sodium hydroxide solutions. Tzeng and Zall (1990) concluded from their studies, with skim and whole milk, that caustic concentration optima were a function of the deposit nature. The variation in concentration optima, found for the membrane systems used here, may be explained by the differences in membrane material and structure as well as solute-membrane interactions.

### 4.4.2 Temperature

In this study the effect of temperature in the range of 20 - 70°C was investigated for the 2 μm sintered stainless steel membrane using a sodium hydroxide concentration of 0.2 wt.%, CFV of 1.59 $ms^{-1}$ and TMP of 0.5 bar. Figure 4.9a shows the maximum % flux recovery values achieved during a 30 minute cleaning operation.

At 20°C the maximum flux recovered was 37% of the measured water flux for a clean membrane under the same conditions. Increasing the temperature by 10°C gave little further benefit, increasing the maximum flux recovery by just 4%. Doubling the temperature to 40°C increased the flux recovery by a factor of 1.5, to give a maximum flux recovery of 55%. A process temperature of 50°C greatly improved flux recovery to give the maximum of 80%. Further increases in temperature resulted in lower maximum flux values.

Figure 4.9b shows a plot of the time taken to reach the maximum % flux recovery v.'s temperature for the sintered stainless steel membrane. Within the range studied, the time taken to reach the maximum % flux recovery showed an exponential decrease

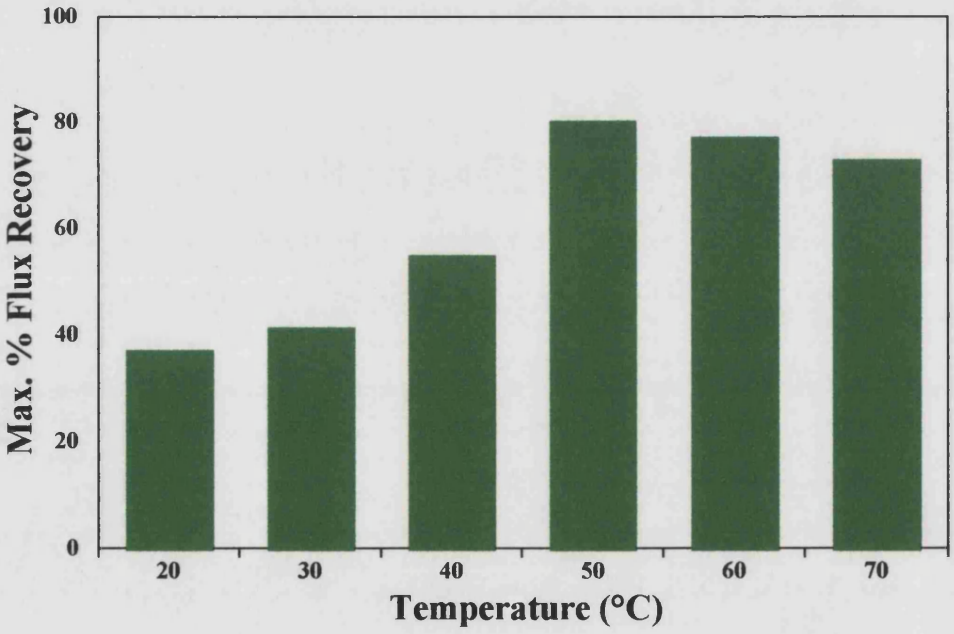



***Figure 4.9a*** *Effect of temperature on maximum % flux recovery for a sintered stainless steel membrane using a 0.2 wt.% sodium hydroxide solution with a TMP of 0.5 bar and a CFV of 1.59 $ms^{-1}$*

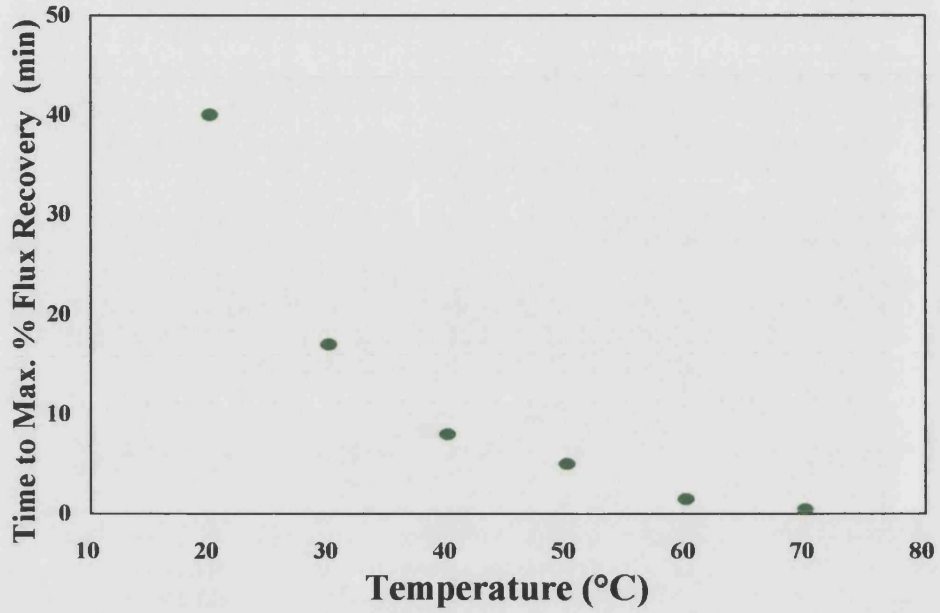



***Figure 4.9b*** *Effect of temperature on time to reach maximum % flux recovery for a sintered stainless steel membrane using a 0.2 wt.% sodium hydroxide solution with a TMP of 0.5 bar and a CFV of 1.59 $ms^{-1}$*

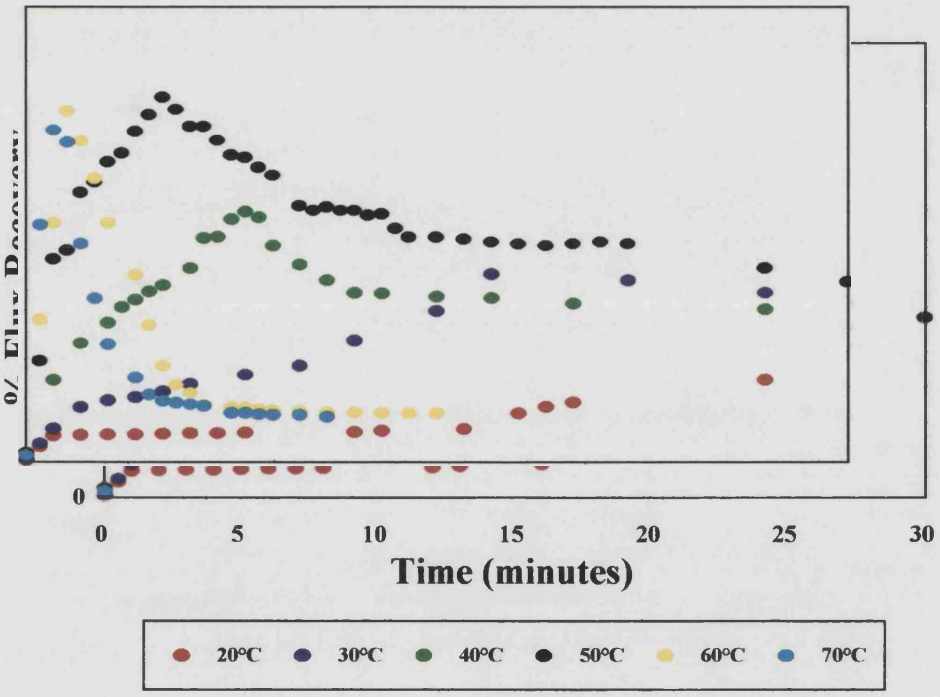



***Figure 4.9c*** *Typical flux recovery curves for a sintered stainless steel membrane using a 0.2 wt.% sodium hydroxide solution with a TMP of 0.5 bar and a CFV of 1.59 $ms^{-1}$*

with increasing temperature. The time taken to reach the maximum % flux recovery fell dramatically from 40 minutes at 20°C to 5 minutes at 50°C. Increasing the temperature further produced faster initial cleaning rates, with the maximum % flux recovery being achieved in just 1 minute at 70°C.

Figure 4.9c shows an overlay plot of the typical cleaning profiles for the sintered stainless steel membrane. The flux recovery curves are of the same form as those described in the previous section. Flux recovery values are initially low and rise to a maximum before declining to a terminal value. Examination of the kinetic data shows that with low cleaning temperatures the maximum % flux recovery values are sustained for the 30 minute cleaning period. As the cleaning temperature is increased beyond 40°C, the rate of decline from the maximum is also increased. Above 60°C the flux has reached its terminal value within 10 minutes.

Two figures, 4.10a and 4.10b are presented to illustrate the effect of temperature upon flux recovery, for a ceramic membrane, using a 0.4 wt.% sodium hydroxide solution as the cleaning agent.

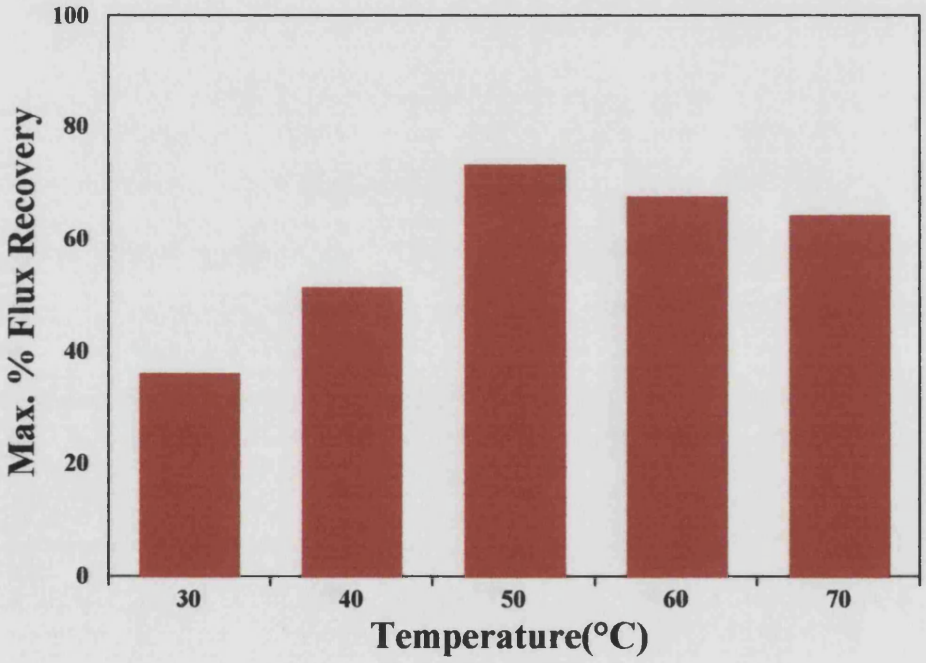



***Figure 4.10a*** *Effect of temperature on maximum flux recovery using a 0.4 wt.% solution for the ceramic membrane with a TMP of 0.5 bar, CFV of 1.59 ms$^{-1}$*

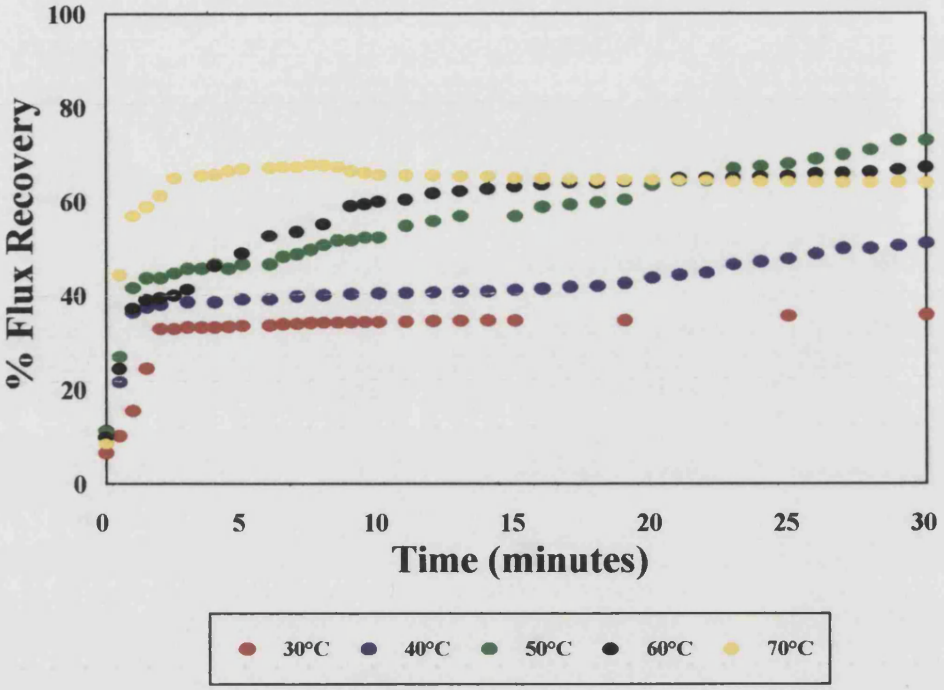



***Figure 4.10b*** *Typical flux recovery curves using a 0.4 wt.% sodium hydroxide solution with the ceramic membrane with a TMP of 0.5 bar and a CFV of 1.59 $ms^{-1}$*

A 36% flux recovery is given when the ceramic membranes are cleaned at 30°C for 30 minutes. A 10°C increase in temperature gives a 15% increase in flux, such that 51% of the available flux is recovered at 40°C. A cleaning temperature of 50°C gives an optimum recovery value of 73%. As with the sintered stainless steel membrane, increases in temperature above this optimum value show a deterioration in the maximum flux recovery achieved.

As with the concentration experiments, a rapid increase in flux recovery during the first two minutes of the cleaning procedure is followed by a more gradual increase for the rest of the cleaning period (Figure 4.10b). Examination of the kinetic data shows rapid flux recovery during the first 2 minutes cleaning for temperatures above 30°C. Cleaning during the next 8 minutes showed a general increase in flux with temperature. After 10 minutes cleaning time, the highest flux recovery was given by

caustic cleaning at 70°C. However, the following twenty minutes produced no further increase in flux for cleaning temperatures above 50°C.

It can be surmised from these results that the flux recovery rate is generally increased with an increase in temperature during the early stages of cleaning. This is due to increased reaction rates and decreased viscosities at higher temperatures. With the low experimental concentrations used here, a linear increase in temperature results a linear decrease in the viscosity and density of the sodium hydroxide solutions (Section 3.1.2). Hence, there is a corresponding increase in the Reynolds Number. The temperatures used here, all resulted in Reynolds Numbers greater than 2100 i.e. turbulent conditions. While there was a linear increase in flux for cleaning temperatures below 50°C the relationship was not consistent beyond this point.

While enzymatic cleaning may exhibit temperature optima, there is little precedent for its occurrence with other chemical-cleaning agents. Both hard surface and membrane cleaning studies have assumed that any increase in temperature will increase cleaning. The reason that temperature optima may not have been noted previously is that the majority of kinetic data has been reported as a function of protein removal and little consideration has been given to the removal of mineral deposits.

Reduced maximum % flux recovery values achieved for temperatures beyond the optimum of 50°C may be explained by the solubility characteristics of calcium. Calcium phosphates are inversely soluble i.e. their solubility decreases with increasing temperature. At temperatures above 50°C there is a significant reduction in the solubility of these compounds, which results in their precipitation.

### 4.4.3 Crossflow Velocity

The importance of crossflow velocity has been investigated over a wide range, 0.26 - 1.90 $ms^{-1}$, at 50°C with a TMP of 0.5 bar. 0.2 wt.% sodium hydroxide was used as the cleaning agent for the sintered stainless steel membranes. 0.4 wt.% sodium hydroxide was used for the cleaning experiments employing the ceramic membrane. The results are presented as the % flux recovery as a function of crossflow velocity (Figure 4.11a) and Reynolds Number (Figure 4.11b), and as overlay plots of the kinetic cleaning data (Figure 4.11c and 4.11d).

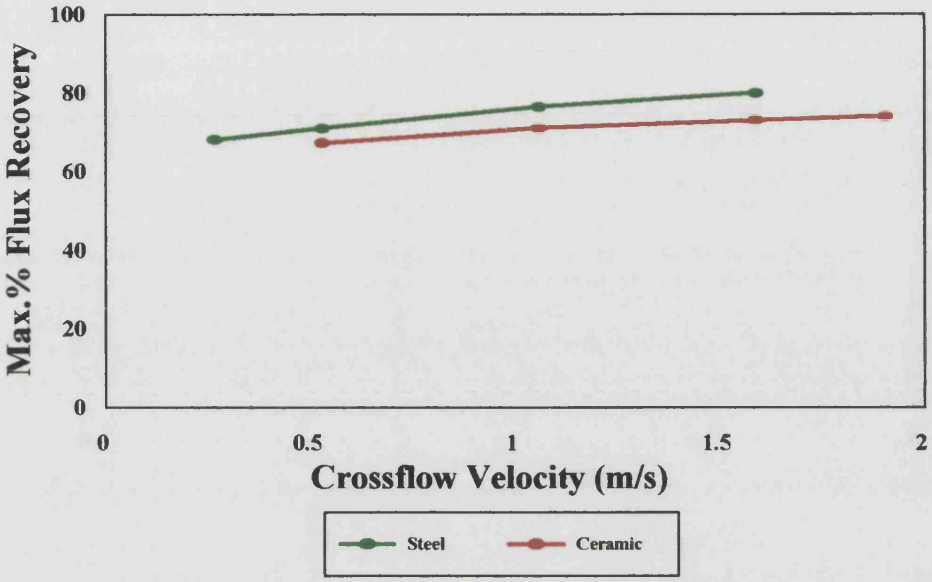



***Figure 4.11a*** *Effect of CFV on flux recovery using a 0.2 wt.% sodium hydroxide solution with the sintered stainless steel membrane and a 0.4 wt.% sodium hydroxide solution with the ceramic membrane at 50°C with a TMP of 0.5 bar.*

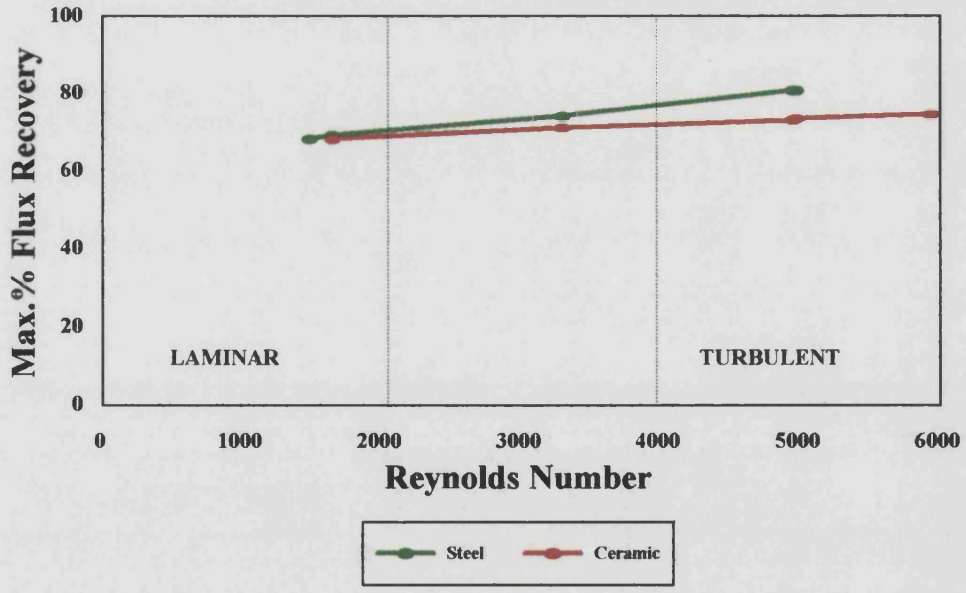



***Figure 4.11b*** *Reynolds Number v.'s % flux recovery, using a 0.2 wt.% sodium hydroxide solution with the sintered stainless steel membrane and a 0.4 wt.% sodium hydroxide solution with the ceramic membrane at 50°C with a TMP of 0.5 bar.*

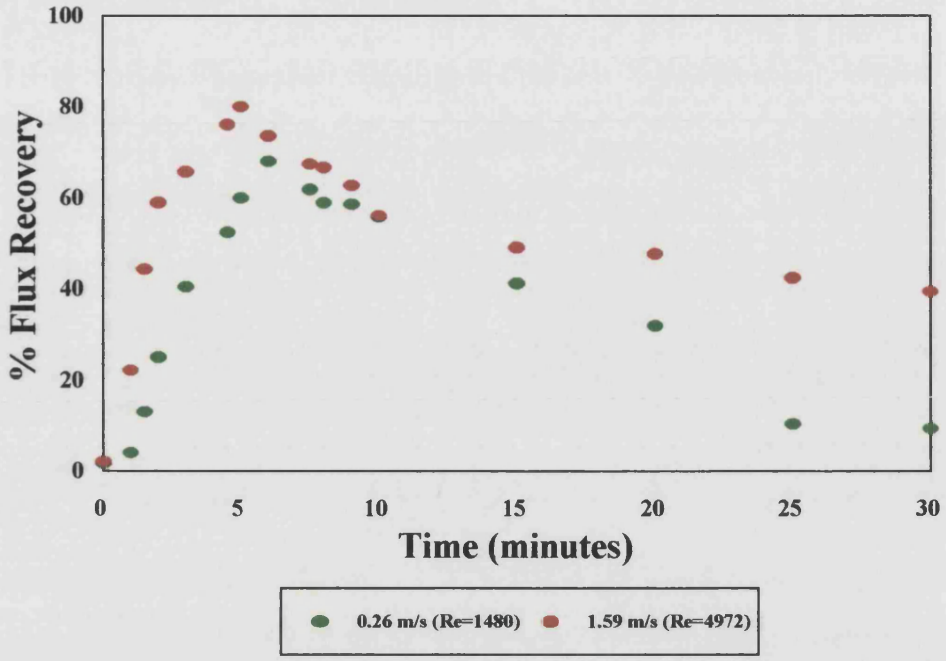



***Figure 4.11c*** *Typical flux recovery profiles for a sintered stainless steel membrane using a 0.2 wt.% sodium hydroxide solution at 50°C, TMP of 0.5 bar.*

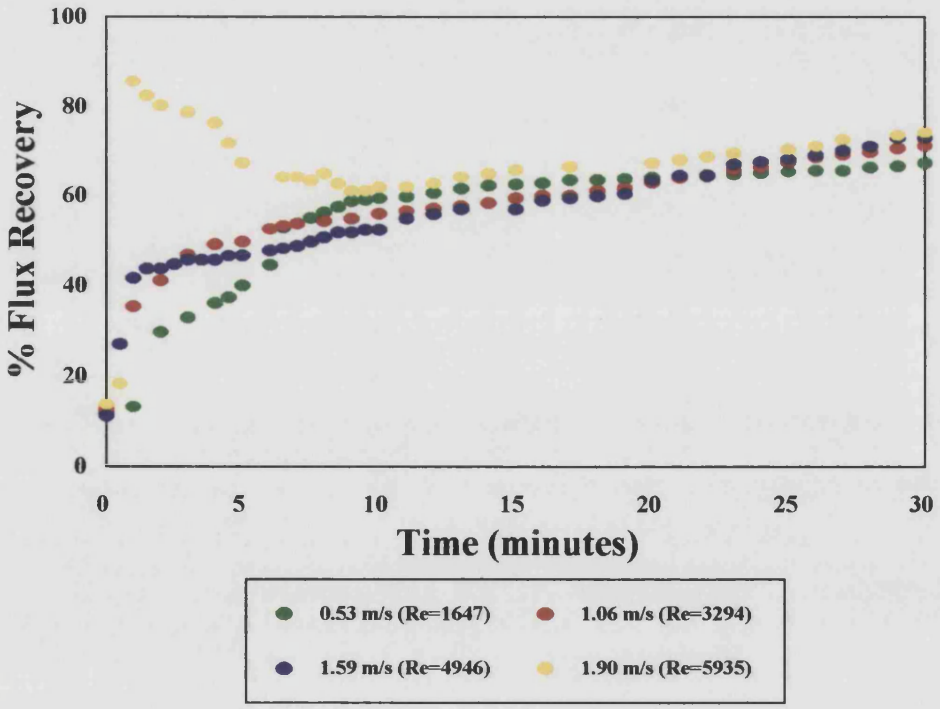



***Figure 4.11d*** *Typical flux recovery profiles for a ceramic membrane using a 0.4 wt.% sodium hydroxide solution at 50°C with a TMP of 0.5 bar.*

Figure 4.11a shows that increasing the CFV has a positive effect on the maximum flux recovery gained in a 30 minute cleaning procedure. Increasing the CFV from 0.26 $ms^{-1}$ to 1.59 $ms^{-1}$ results in a 12 % increase in flux for the sintered stainless steel membrane. However, an increase of just 7% was found by increasing the CFV from 0.53 $ms^{-1}$ to 1.90 $ms^{-1}$ for the ceramic membrane.

Plotting the maximum % flux recovery against Reynolds Number (Figure 4.11b) shows that the flux recovery rate increases smoothly from laminar to turbulent flows, during the cleaning of both membrane systems.

Examination of the cleaning profiles for the sintered stainless steel membrane (Figures 4.11c) shows that increasing the velocity from laminar to turbulent flow increased the recovery rate. Nevertheless, increasing the flow rate only reduced the time taken to reach the maximum % flux recovery from 6 to 5 minutes. However, it had a positive effect on the final flux recovery value. Increasing the CFV reduced the rate of decline from the peak flux value, with the implication that fluid mechanics are important in determining the final flux in this system.

The overlay plots for the ceramic membrane (Figure 4.11d) demonstrate that increasing the CFV increased the rate of flux recovery during the first stage of the cleaning process, but the change from laminar to turbulent flow conditions had little effect on the final flux recovery value. Cleaning at 1.90 $ms^{-1}$ gave an unusual flux recovery profile. The result suggests that the deposit was 'lifted' from the membrane surface which gave an immediate flux recovery of 80%. It seems that the material was then redeposited, as the cleaning profile then follows the synchronous recovery path of the other experiments.

Increasing the cleaning fluid velocity always enhanced the flux recovery, in both membrane systems. As the CFV was increased, and the flow regime changed from laminar to turbulent flow, there was a gradual increase in the cleaning rate.

### 4.4.4 Transmembrane Pressure

Flux recovery was examined using TMP's of 0, 0.5 and 1 bar. 0.2 wt.% sodium hydroxide was used as the cleaning agent for the sintered stainless steel membranes. 0.4 wt.% sodium hydroxide was used for the cleaning experiments employing the ceramic membrane. Results are displayed as the maximum % flux recovery v.'s

transmembrane pressure (Figure 4.12a), and as overlay plots of the cleaning kinetics for the sintered stainless steel (Figure 4.12b) and ceramic (Figure 4.12c) membranes.

A maximum flux recovery of 94 % was given for the sintered stainless steel membrane after cleaning with a zero TMP for 30 minutes. This value was reduced by 14% when a fouled membrane was cleaned using a 0.5 bar TMP. There was a further reduction of 8% when a TMP of 1 bar was applied, reducing the maximum % flux recovery to 72%.

97 % of the available flux was recovered when the ceramic membranes were cleaned with out an applied TMP. There was a reduction in the flux recovery of 24% when a TMP of 0.5 bar was used to clean the WPC fouled membranes. Just 62 % of the flux was recovered when a TMP of 1 bar was used.

Examination of the kinetic data, revealed that 80% of the available flux was recovered in first 2 minutes of the cleaning procedure, when zero TMP was employed (Figure 4.12b). Pressure appeared to have little effect on the initial removal rate, but it did affect the rate of decline from the maximum. As the TMP increased so the rate of decline from the maximum increased.

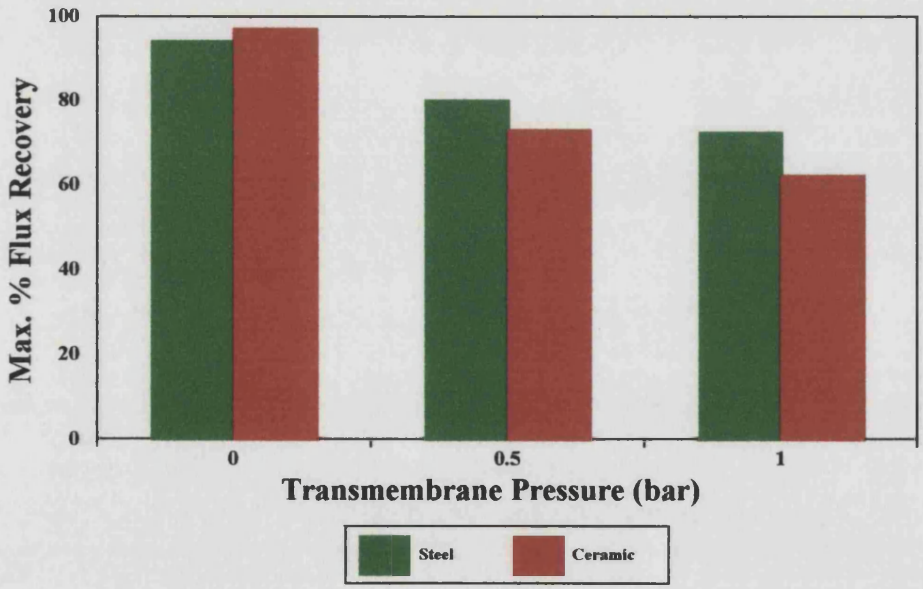



***Figure 4.12a*** *Effect of TMP on maximum % flux recovery for a sintered stainless steel membrane cleaned with 0.2 wt.% sodium hydroxide and for a ceramic membrane cleaned with 0.4 wt.% sodium hydroxide at 50°C with a CFV of 1.59 $ms^{-1}$*

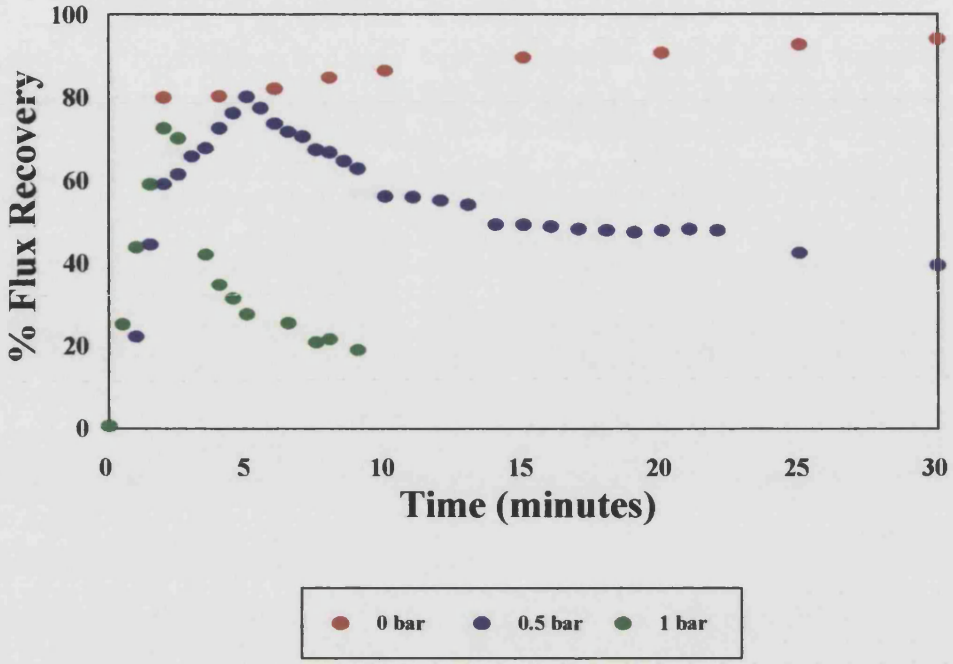



***Figure 4.12b*** *Effect of TMP on flux recovery for a sintered stainless steel membrane using a 0.2 wt.% sodium hydroxide at 50°C with a CFV of 1.59 $ms^{-1}$*

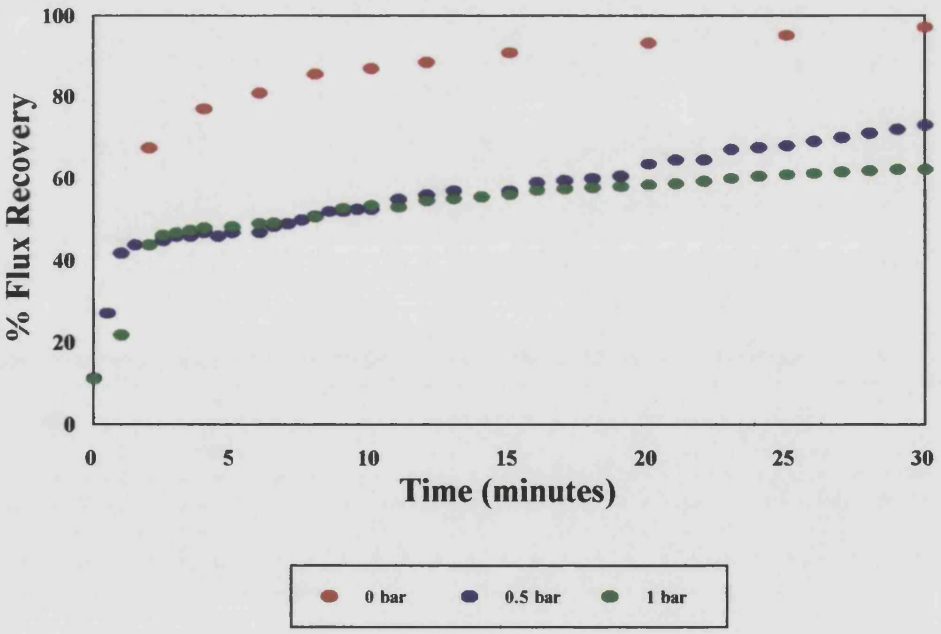



***Figure 4.12c*** *Effect of TMP on flux recovery for a ceramic membrane using 0.4 wt.% sodium hydroxide at 50°C with a CFV of 1.59 $ms^{-1}$*

The application of a positive transmembrane pressure during cleaning had a detrimental effect. Zero TMP produced the highest flux recovery values after a 30 minute cleaning period, for both the sintered stainless steel and the ceramic membranes. The flux recovery after cleaning was sustained during the rinsing phase, for both systems. The application of a TMP greater than zero resulted in lower flux recoveries. For maximum cleaning efficiency, permeate lines should be closed during the early stages of the cleaning process or until all surface deposits have been removed.

In a system operating with a positive transmembrane pressure, compressive forces may hinder the removal of surface deposits. As a result of these observations further experiments were carried out to investigate the effect of sodium hydroxide concentration on flux recovery employing zero TMP. Figure 4.13 plots sodium hydroxide concentration against the maximum flux recovery given in a 30 minute cleaning period.

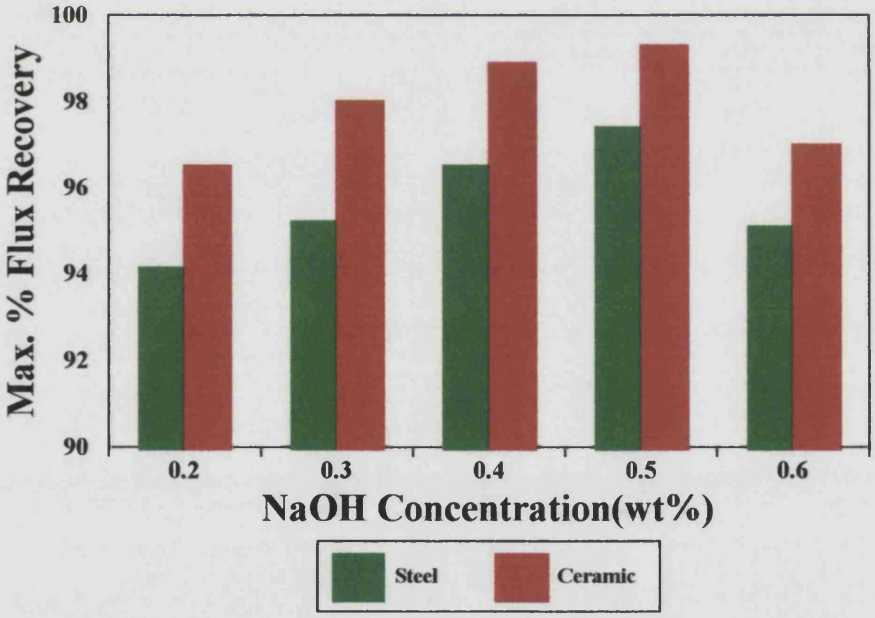



***Figure 4.13*** *Effect of sodium hydroxide concentration on the maximum % flux recovery with zero TMP at 50°C with a CFV of 1.59 $ms^{-1}$ for sintered stainless steel and ceramic membranes.*

The maximum % flux recovery was considerably higher, for both membrane systems, when cleaning without a TMP. The results show that the optimum sodium hydroxide concentration for flux recovery was 0.5 wt.%. This optimum value is the same as that found for the removal of WPC deposits from hard surfaces [Fryer and Bird (1991), Bird (1993)]. This indicates that the concentration optimum for the removal of WPC deposits is generic. Any observed deviations are due to the membrane itself, or the operating conditions used to cleaning it. A more complex matrix of experiments is required to elucidate the interactive nature of the cleaning parameters.

## 4.5 VISUALISATION OF THE CLEANING PROCESS

In addition to quantitative experiments, information concerning cleaning was obtained by qualitative observation of the membrane samples. Direct visualisation of the cleaning process was not possible as the stainless steel module precluded observation. Here, removal of samples, and observation with the naked eye, allowed the presence of gross deposits to be described. The use of (i) Scanning Electron Microscopy and (ii) x-ray microanalysis has allowed deposit structure to be related to flux recovery.

Multiple cleaning experiments were performed on 0.2 μm sintered stainless steel membranes fouled with 3.5 wt.% WPC solution at 50°C, to provide 'snap-shots' of the cleaning performance at different times. Multiple cleaning runs, with 0.2 wt.% sodium hydroxide, at 50°C with a CFV of 1.59 $ms^{-1}$ and TMP of 0.5 bar, were stopped at different time intervals in the 30 minute cleaning procedure.

Observation of the sintered stainless steel membrane surface with the naked eye easily revealed gross deposits because of the contrast between the membranes' grey colour and the cream or white WPC deposits (not shown here). Use of a light microscope estimated the thickness of these deposits to be no more than 0.3 mm thick.

The fouling procedure produced wet samples of a spongy deposit, which was pale cream in colour. Contact with sodium hydroxide reduced both the thickness and coverage of the deposit with time. Gross deposits became progressively whiter in colour over the cleaning period and more 'chalky' in texture. After the 30 minute cleaning period no surface deposits could be seen.

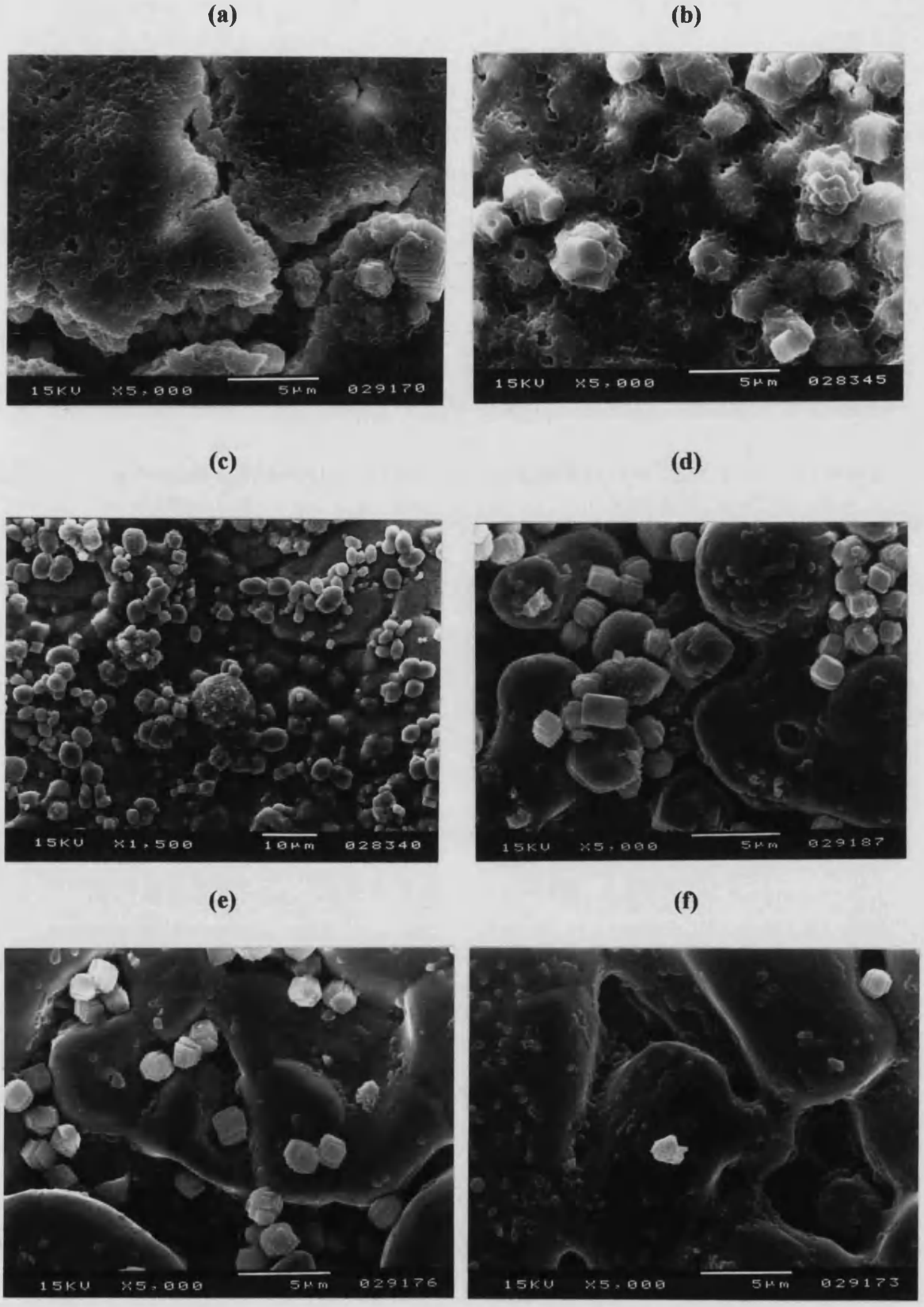



***Figure 4.14*** *SEM's showing deposit removal from a sintered stainless steel membrane using 0.2 wt.% NaOH (a) t=0 minutes, (b) t=1 minute, (c) t=4 minutes, (d) t=6 minutes, (e) t=10 minutes, (f ) t=30 minutes.*

SEM's show deposit removal over a 30 minute cleaning period (Figures 4.14a - f). At time zero, the micrographs revealed a severely fouled membrane surface. The 'sheet-like' deposit was removed within the first minutes of the cleaning process to reveal a deposit of aggregates and minerals embedded in a matrix (t=1 minutes). With continued caustic cleaning the matrix and aggregates were removed (t=4 minutes), such that the membrane appeared relatively free of organic deposits (t=6 - 10 minutes). After 30 minutes caustic cleaning only mineral deposits could be seen on the surface of the membrane. Examination of membranes cleaned with 0.5 wt.% Ultrasil 11 showed little evidence of mineral deposit after 30 minutes cleaning (Figure 4.15). A micrograph of the deposit when it had been contacted with a 1.0 wt.% sodium hydroxide solution for 2 minutes, revealed changes in the surface morphology (Figure 4.16) compared to the cleaning with 0.2 wt.% sodium hydroxide.

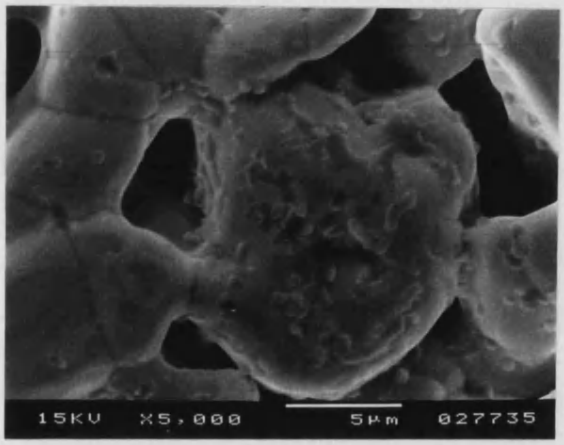



***Figure 4.15*** *SEM of membrane cleaned with Ultrasil 11 for 30 minutes*

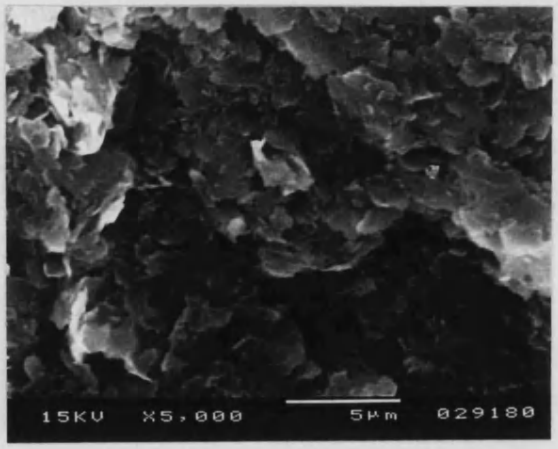



***Figure 4.16*** *SEM of membrane cleaned with 1.0 wt.% sodium hydroxide for 2 minutes.*

Qualitative analysis of the membrane surface using x-ray microanalysis confirmed what was seen with the SEM. At time zero, the surface was primarily organic (Figure 4.17a). Removal of these overlaying proteins revealed a deposit of aggregates and minerals, which had a high calcium content (Figure 4.17b). Calcium, was the primary foulant after 10 minutes cleaning (Figure 4.17c). After caustic

cleaning a small amount of organic material was still detected. Cleaning with Ultrasil 11 resulted in a membrane that was free of mineral deposits, but a small amount of organic material could still be detected (Figure 4.17d).

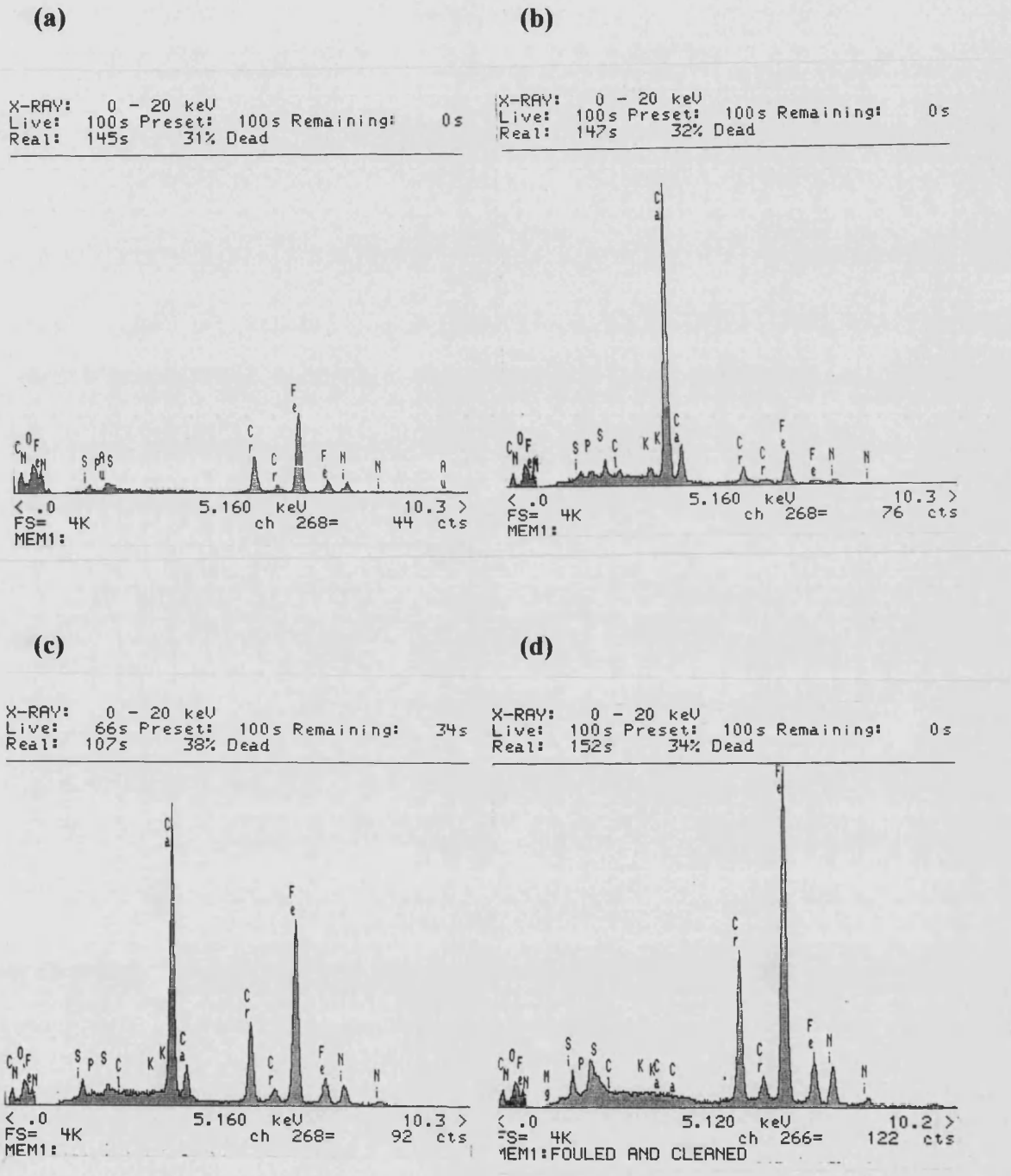



*Figure 4.17 X-ray micrographs of the membrane surface after (a) t=0 minutes, (b) t=1 minute, (c) t=10 minutes cleaning with 0.2 wt.% sodium hydroxide. (d) t=30 minutes cleaning with 0.5 wt.% Ultrasil 11*

The removal of the 'sheet-like' proteins, within the first minutes of contact with sodium hydroxide, reduced the deposit's resistance to flow, and a rapid increase in flux is observed. The swelling of the deposit, and the removal of aggregates and protein matrix from the membrane surface, caused an increase in flux to a maximum value. As the membrane was essentially free of surface deposits after this period, any decline in flux may be explained by the presence of in-pore material.

## 4.6 EFFECT OF CLEANING ON MEMBRANE DURABILITY

The durability of the 0.2 μm ceramic and Supor 100 polyethersulphone MF membranes was tested against chemical and thermal attack. Small strips, 3cm x 2cm, were immersed in sealed glass vials of distilled water or solutions of 0.5 wt.% sodium hydroxide, 2.0 wt.% sodium hydroxide or 0.5 wt.% $HNO_3$, at 50 and 80°C. Samples were removed after a 320 hour contact period, and photographed using SEM techniques to detect any physical damage.

Figure 4.18a shows a micrograph of a new 0.2 μm ceramic membrane, supplied by NWW Acumem Ltd, which has been used for comparison purposes with test membrane samples.

The SEM's showed that the ceramic membrane was damaged, after it was contacted with distilled water under static conditions, at 50 and 80°C (Figure 4.18b). The micrograph revealed that the surface had started to degrade. The ceramic material showed pitting on the raised areas of the mesh structure.

Using concentrations of 0.5 wt.% sodium hydroxide caused pitting and flaking of the raised areas of the membrane mesh, at both 50 (Figure 4.18c) and 80°C. Increasing the sodium hydroxide concentration to 2.0 wt.% increased the damage, causing further cracking and detachment of the ceramic matrix. This was again focused on the raised portions of the mesh structure, at both 50 and 80°C (Figure 4.18d). The material within the mesh structure appeared to remain intact.

Contacting the ceramic membrane with a 0.3 wt.% $HNO_3$ solution for 320 hours, in this static system, appeared to result in little degradation of the actual membrane matrix. However, precipitation of mineral deposits did occur at 50°C (Figure 4.18e), which increased to form 'crust-like' deposits at 80°C.

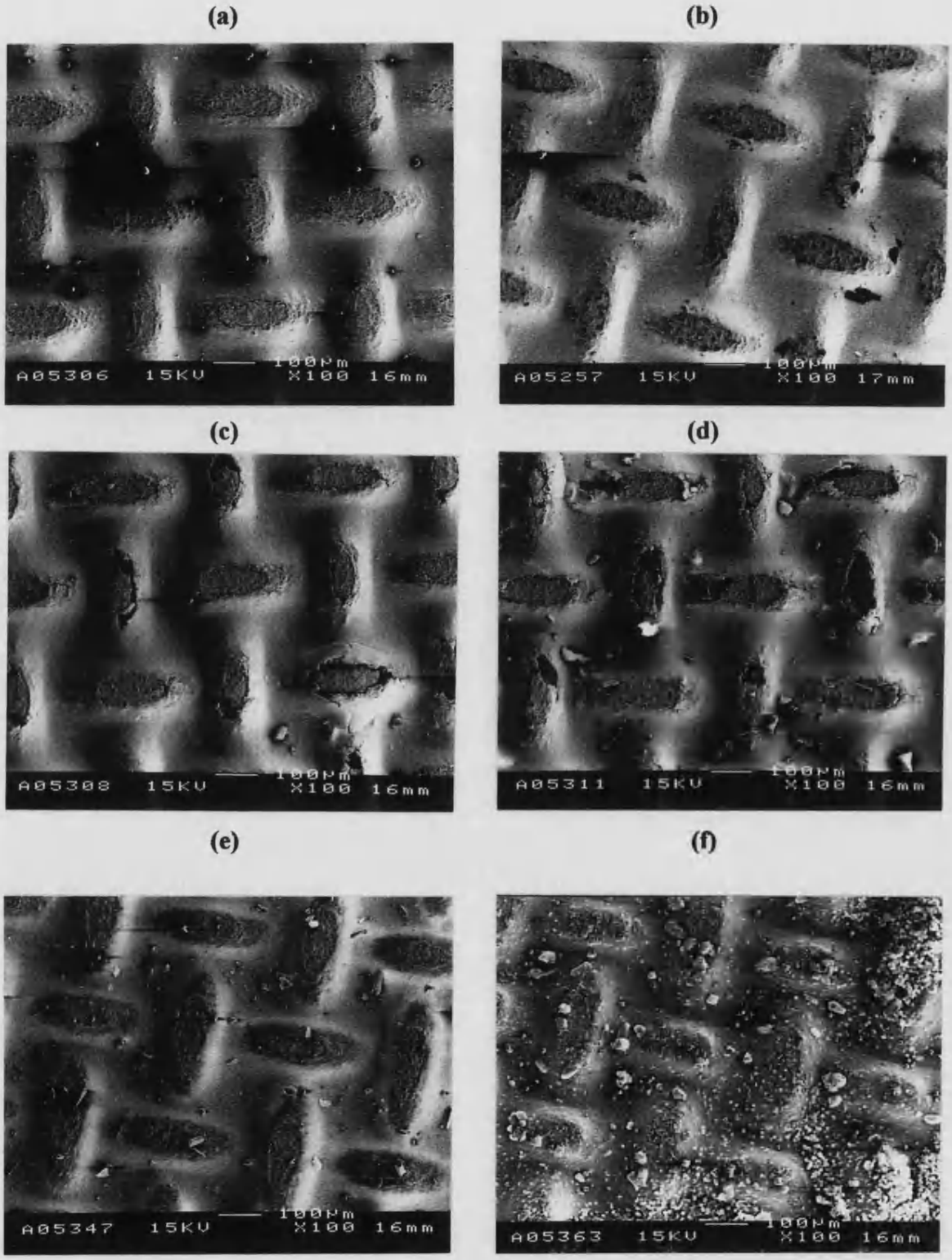



***Figure 4.18*** *SEM's showing degradation of the ceramic membrane (a) pristine membrane (b) distilled water at 80℃, (c) 0.5 wt.% sodium hydroxide at 50℃, (d) 2.0 wt.% sodium hydroxide at 80℃, (e) 0.5 wt.% nitric acid at 50℃, (f) 0.3 wt.% nitric acid at 80℃.*

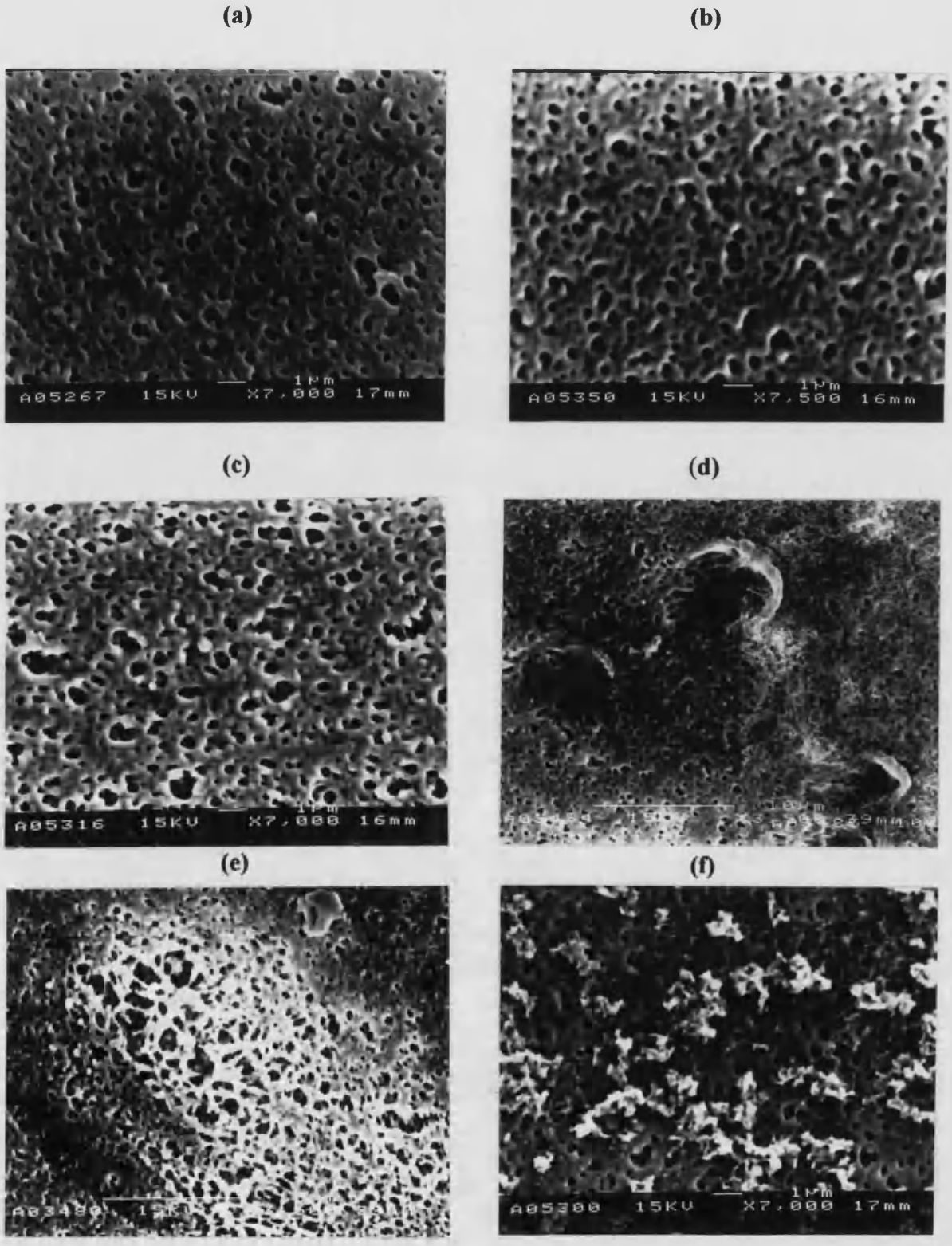



***Figure 4.19*** *SEM's showing degradation of the PES membrane (a) pristine membrane (b) distilled water at 80℃, (c) 0.5 wt.% sodium hydroxide at 80℃, (d) 2.0 wt.% sodium hydroxide at 50℃, (e) 2.0 wt.% sodium hydroxide at 80℃, (f) 0.3 wt.% nitric acid at 80℃.*

Figure 4.19a shows the pristine Supor 100 PES membrane as supplied by Gelman Sciences Ltd. The membrane has a smooth surface, with a high porosity and a wide pore size distribution.

Examination of the PES membrane showed the effect of prolonged contact with chemical cleaning agents, at elevated temperatures, in a static system. Contacting the membrane with distilled water at 50°C caused little damage. At 80°C (Figure 4.19b) there was some pore enlargement, which gave the appearance of increased surface porosity.

Contact experiments with 0.5 wt.% sodium hydroxide solution also caused little damage at 50°C. Again, some pore enlargement was seen at 80°C (Figure 4.19c), similar to that found with water at the same temperature.

After 320 hours contact with 2.0 wt.% sodium hydroxide at 50°C distinct areas of attack could be distinguished on the PES membrane (Figure 4.19d). At 80°C the membrane damage was so severe that areas of the surface had 'blown' (Figure 4.19e). Damage caused localised expansion of the pore structure and a breakdown of the polymeric matrix.

0.3 wt.% nitric acid had little effect on the apparent pore size of the membrane either at 50 or 80°C (Figure 4.19f). However mineral deposition in this static system built up as the temperature increased.

A period of 320 hours corresponds to approximately 1 hours cleaning for every operational day in a production year. PES membranes are believed to be resistant to chemical and thermal degradation for pH 1-13 and for temperatures up to 80°C. Ceramic membranes, in particular, are supplied as being highly resistant to severe chemical and thermal conditions. The results presented show that, in this static system, even moderate cleaning agents and temperatures cause irreversible damage to the membrane structure. It is expected that this damage would affect the membranes performance, and have consequences for the membranes operational lifetime.

No permeability measurements were taken for a qualitative assessment of how the cleaning agent deterioration affected the performance of these membranes.

## 4.7 MULTIPLE FOULING AND CLEANING CYCLES

In this section, standard conditioning, cleaning and restoration procedures were assessed for their effect on membrane fouling.

A new Supor 100 PES MF membrane was compressed by circulating a 50 mM solution of sodium nitrate at 50°C with a TMP of 1.5 bar and a CFV of 1.59 $ms^{-1}$ for 1 hour. The membrane was then preconditioned and compressed by cleaning with 0.5 wt.% sodium hydroxide for 1 hour using the same process conditions. The membrane was fouled and restored through multiple cycles, using the standard conditions as described in Chapter 3.

Figure 4.20a shows an overlay plot of flux v.'s transmembrane pressure for the water flux values taken after each procedure in the cycle. It can be seen from the flux values that the water permeability of the membrane was affected by the conditioning procedures carried out. Compressing the membrane reduced the original water flux by 21%. The following preconditioning procedure with sodium hydroxide increased the flux by about 90 $kg/hm^2$ (9.5%) at 1 bar pressure.

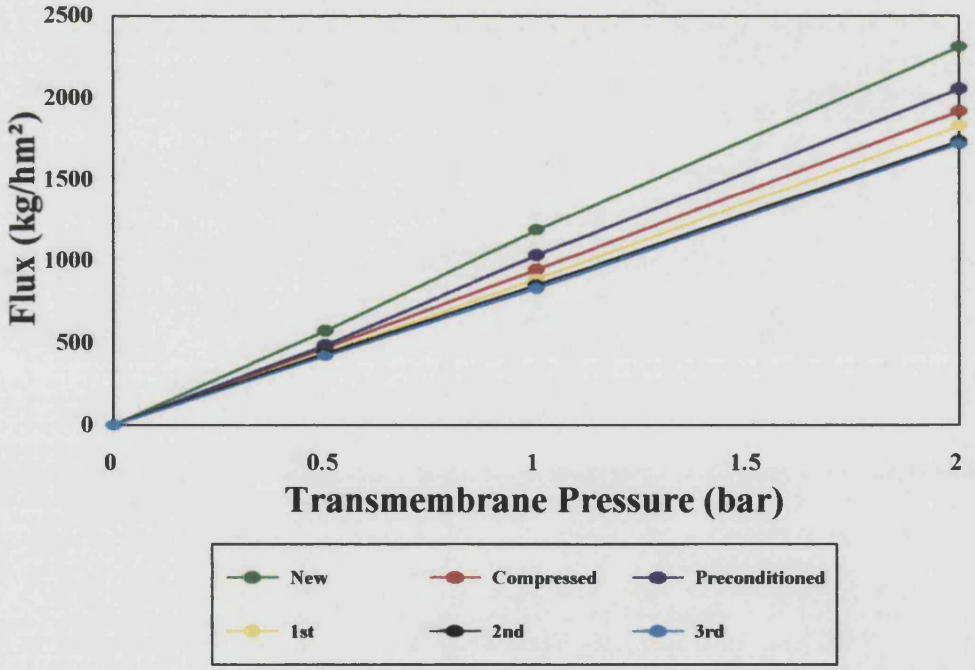



***Figure 4.20a*** *Comparison of water flux values through multiple fouling and cleaning cycles using a PES membrane. Water flux measurements taken at 50℃ with a CFV of 1.59 $ms^{-1}$.*

The first fouling-restoration cycle reduced the preconditioned membrane flux by about 12%. The second cycle reduced it by a further 6%. By the third cycle an additional decrease of only 1% was seen because membrane performance was stabilised.

Figure 4.20b compares the kinetics of successive fouling runs. Examination of the data shows that the highest flux values were for the first fouling run. The flux during the next fouling run was reduced by about 20%. There was an increase in permeability with each of the fouling runs that followed this, suggesting that the fouling mechanism changed with each successive run.

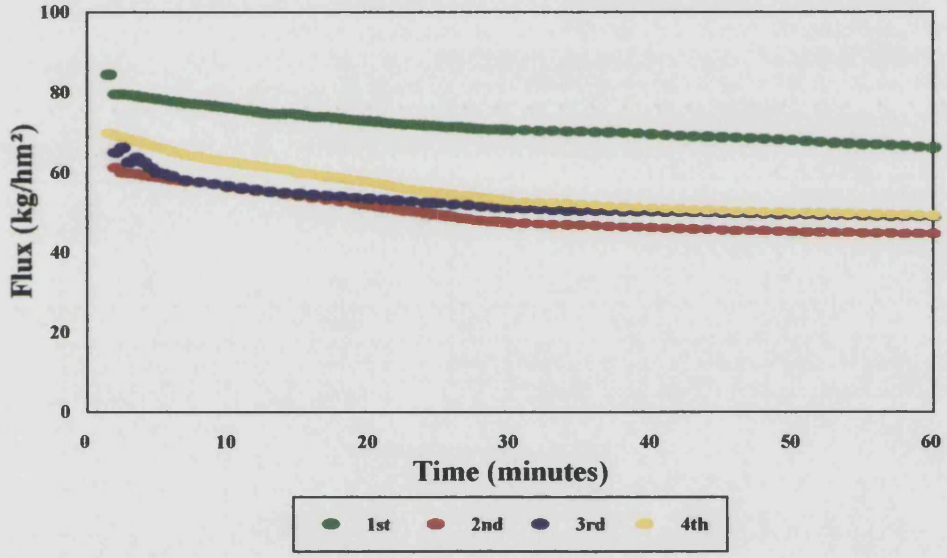



***Figure 4.20b*** *Comparison of fouling kinetics through multiple fouling cycles for a PES membrane using a 3.5 wt.% WPC solution at 50℃ with a CFV of 1.04 $ms^{-1}$ and TMP of 1.0 bar.*

The observed differences in both water flux and fouling kinetics suggests that caustic based cleaning agents modify the membrane. Several researchers have noted an increased water permeability with polymeric membranes contacted with cleaning agents. Chong *et al* (1985) found that contacting polysulphone UF membranes with sodium hydroxide and surfactant solutions significantly increased the water flux, while solutions such as nitric acid and EDTA caused only slight variations in membrane permeability. Nystrom and Zhu (1996) found that cleaning modified, hydrophilic

polysulphone membranes with 0.5 wt.% sodium hydroxide at 80°C increased the water flux by 67%. Using oxalic acid as a preconditioning agent caused a 49% water flux increase, for the same membrane. Their results indicated that these compounds had little effect on hydrophobic polysulphone UF membranes that were also tested. Bartlett (1996) found that Ultrasil 10 increased the water flux of compressed PES UF membranes by 33% when used at 50°C in a stirred cell. The results suggested that these cleaning compounds may increase flux by opening up the pore structure of the membrane. In the previous section, SEM's show that continued use of sodium hydroxide caused an increase in the observed pore diameters of PES membranes.

Polyethersulphone carries a negative charge, which may be increased by cleaning with chemicals such as NaOH and Ultrasil 11 [Nystrom and Zhu (1996)]. The increased negative charge may cause electrostatic repulsion of proteins during the first fouling procedure. Reduced protein-membrane interaction would give rise to a higher permeation rate during the first fouling procedure.

Adsorption of protein to the membrane surface, during the first fouling procedure, may cause further physiochemical modifications that could mask the intrinsic properties of the membrane surface. FTIR analysis of hydrophobic polysulphone membranes [Nystrom and Zhu (1996)], and hydrophilic PES UF membranes [Bartlett (1996)], revealed that after the filtration of BSA, sodium hydroxide did not remove all the fouling. Further permeability measurements are as a result of solute interactions with the adsorbed protein, and not the membrane material.

As previously discussed, the membrane performance is strongly dependent on the extent of protein adsorption and the position of the foulant. As the MF membrane is permeable to whey proteins the initial decline in the permeation rate is controlled by protein deposition in the pores of the membrane. Progressive blocking of the membrane pores, with each fouling run, caused a shift in the fouling mechanism until the membrane was stabilised.

## 4.8 FOULING AND CLEANING SYNERGY

Flux recovery was used as the main criterion to assess the effect of fouling conditions on membrane cleanability. This preliminary study was carried out using Supor 100 PES MF membranes, fouled with a 3.5 wt.% reconstituted protein solution. Temperatures of 20, 50 and 70°C were employed to generate deposits of different

fouling tendency, morphology and permeation characteristics. The effect of fouling using TMP's of 0.5, 1.0 and 2.0 bar and CFV's of 0.53, 1.04 and 1.59 $ms^{-1}$ were evaluated after microfiltration runs of 1 hour. HPLC was employed to evaluate changes in permeate quality for each fouling runs.

### 4.8.1 Effect of Fouling Temperature on Cleanability

Figure 4.21a shows an overlay plot of flux v.'s time for the fouling procedures at temperatures of 20, 50 and 70°C. It can be seen from the flux values that the temperature of the bulk solution has a direct effect on the time to reach the terminal flux.

At lower temperatures the viscosity of the fouling solution was higher (at 20°C $\mu$=0.00179 $kgm^{-1}s^{-1}$) and fouling was rapid. Increasing the temperature to 50°C decreased viscosity ($\mu$=0.00146 $kgm^{-1}s^{-1}$) and caused an increase in flux. Increasing the foulant temperature to 70°C caused an initial increase in flux, as the viscosity of the solution was reduced by half ($\mu$=0.000691 $kgm^{-1}s^{-1}$).

The fouling tendency of the solution and the morphology of the deposit formed can explain these results. At 20°C little aggregation occurs, as a consequence, in-pore deposition was followed by the rapid formation of a fine, heavily granulated cake deposit. No fouling mechanism dominate at 50°C (Section 4.1). Aggregates, which block the larger pores, and minerals were embedded in a matrix of finer material. Increasing the temperature to 70°C increased the interaction of free proteins with aggregates [Xiong *et al* (1993)] and the deposition of calcium salts. Hence, the transmission of β-LG and BSA was severely reduced (Figure 4.22f). As the temperature was increased from 20 - 70°C there was a general decrease in the transmission of both α-LA and β-LG.

Figure 4.21b demonstrates how the fouling process, and the nature of the resulting deposit, affected membrane cleaning. Examination of the flux recovery profiles showed that there was a rapid increase in flux on contact with sodium hydroxide, for the membranes fouled at both 20 and 50°C. In contrast, flux recovery was slow during the cleaning of membranes fouled at 70°C. There was a lag period of about 2.5 minutes before any improvement in flux occurred.

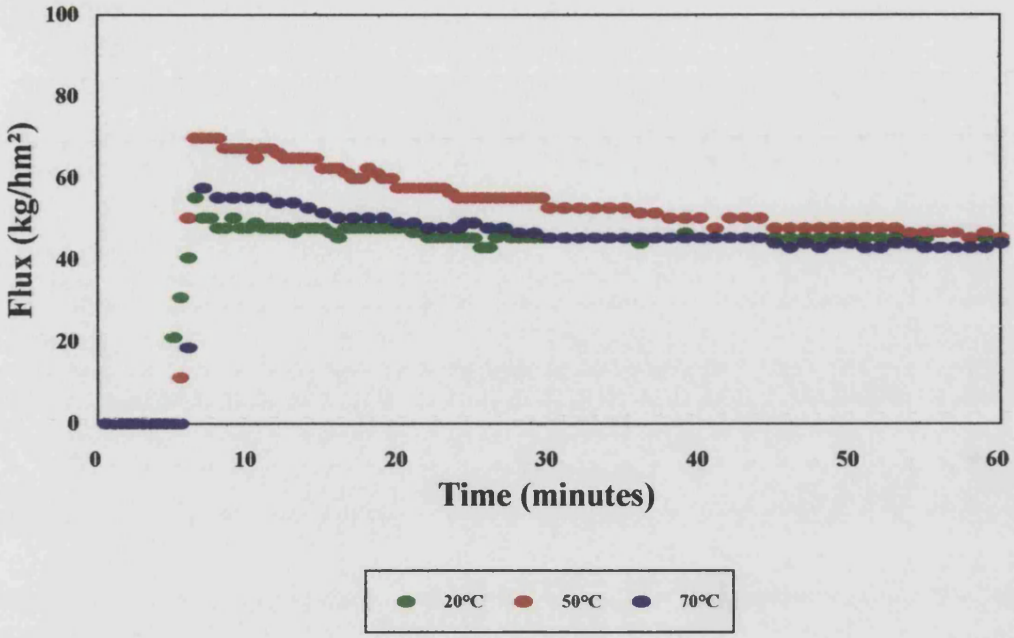



***Figure 4.21a*** *Effect of fouling temperature on flux decline for a Supor 100 PES membrane using a 3.5 wt.% protein solution with a TMP of 1 bar and CFV of 1.04 $ms^{-1}$*

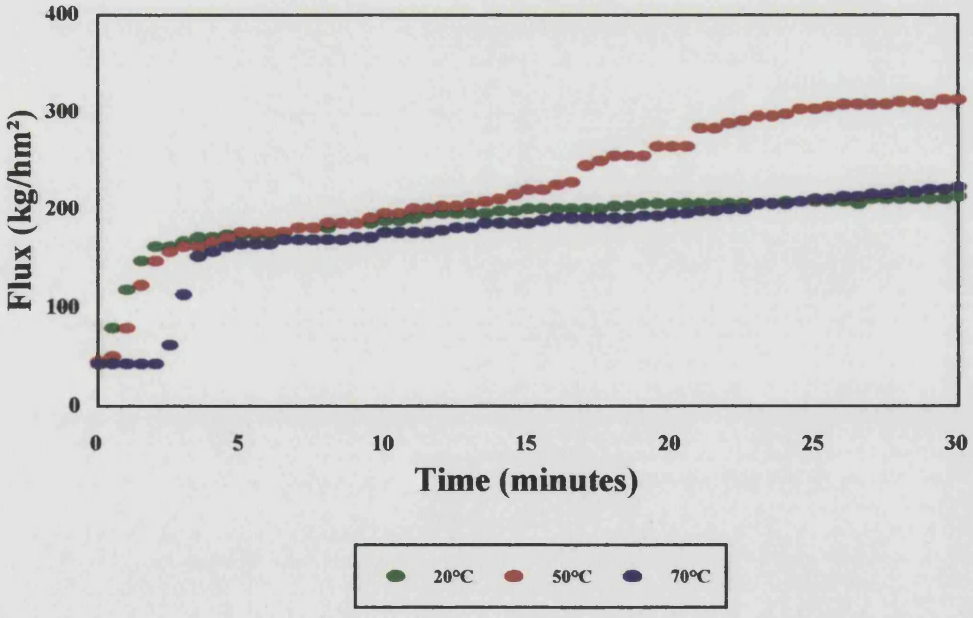



***Figure 4.21b*** *Effect of fouling temperature on flux recovery for a Supor 100 PES membrane cleaned with 0.4 wt.% sodium hydroxide at 50°C, TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$*

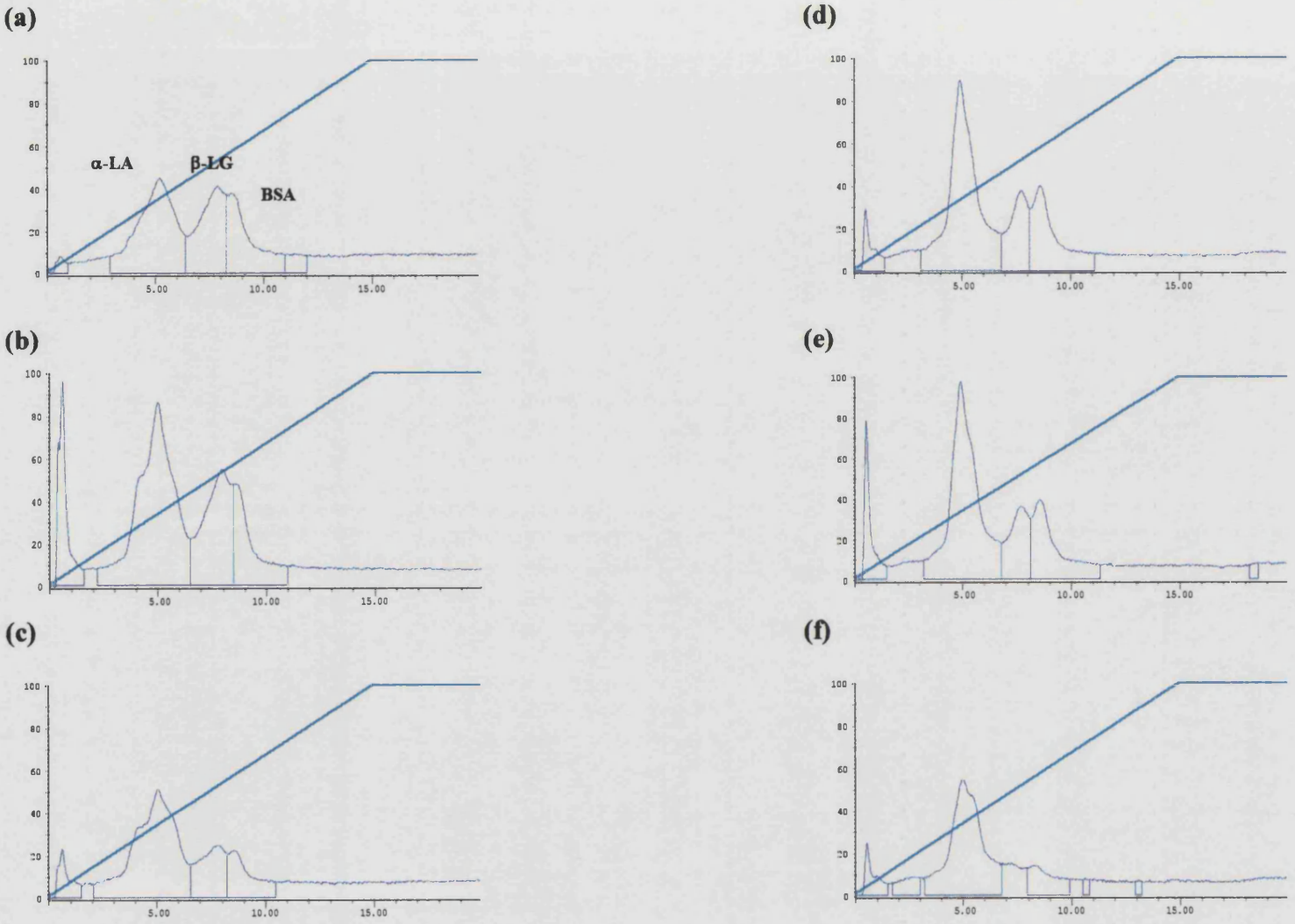



***Figure 4.22*** *HPLC analysis of whey proteins in permeate (a) 3.5 wt.% whey standard at 50℃ (b) 50℃ with TMP of 0.5 bar , (c) 50℃ with TMP of 2 bar, (d) 20℃ with TMP of 1 bar, (e) 50℃ with TMP of 1 bar, (f) 70℃ with TMP of 1 bar. 6 mV full scale deflection.*

The flux recovery values suggest that surface proteins were readily removed from membranes fouled using temperatures of 20 and 50°C. The removal of large aggregates during the later stages of cleaning would account for the sharp increase in flux observed at 50°C. Increased pore fouling with the lower fouling temperature meant that the rate of flux recovery was less successful in the later stages of cleaning. At 70°C the increased retention of proteins, and the precipitation of calcium salts, gave a deposit that was difficult to remove from both the membrane surface and pores.

### 4.8.2 Effect of Fouling Transmembrane Pressure on Cleanability

Figure 4.23a shows an overlay plot of flux v.'s time for the filtration of a 3.5 wt.% protein solution at 50°C with a CFV of 1.04 $ms^{-1}$, for TMP's of 0.5, 1.0 and 2.0 bar.

The tendency for the terminal flux to be established more rapidly at lower filtration pressures was clearly demonstrated. Increasing the TMP to 1.0 bar give an initial increase in flux, compared to 0.5 bar. This advantage was quickly lost as flux rapidly declined with time. Employing a TMP of 2.0 bar gave a permeation rate that was 33% higher than that given with an applied pressure of 0.5 bar.

The kinetic fouling data can be explained in terms of protein retention and deposit formation. Kim *et al* (1992) showed that, in general, flux decreased as retention increased. Fouling with a 0.5 bar TMP increased protein transmission characteristics (Figure 4.22b), and a finer, more dense, cake was formed. Tarleton and Wakeman (1994) found that increasing the pressure increased the pore fouling,. With a fouling TMP of 2 bar, material was brought to the membrane surface at a faster rate and deposit formation was rapid. This caused a reduction in the transmission of proteins (Figure 4.22c).

It is interesting to note that a time lag was observed during the first few minutes of filtration. Fane's research group in Sydney found that, for some permeable membranes, an increase in protein rejection did not occur until after a few minutes, despite an immediate drop in UF flux. In fact, rejection was initially raised before dropping to a low value and a subsequent gradual increase [Suki *et al* (1984), Kim *et al* (1992)]. This time lag has been attributed to the chromatographic adsorption of solute onto, and within, the membrane pores. This phenomenon may explain our lag period.

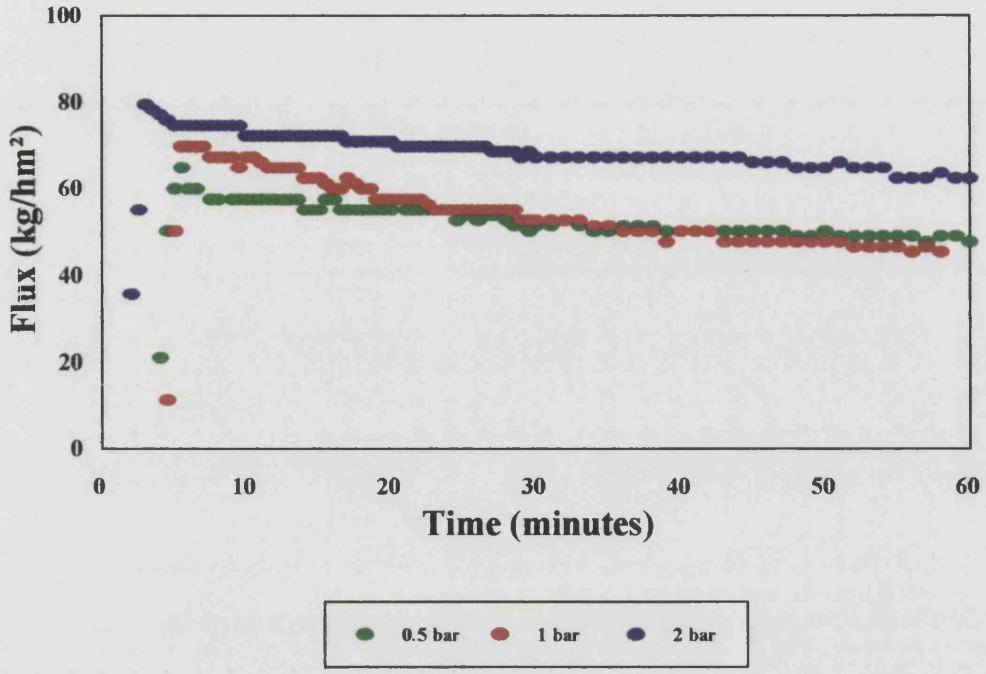



***Figure 4.23a*** *Effect of fouling TMP on flux decline for a Supor 100 PES membrane using a 3.5 wt.% protein solution at 50°C with a CFV of 1.04 $ms^{-1}$*

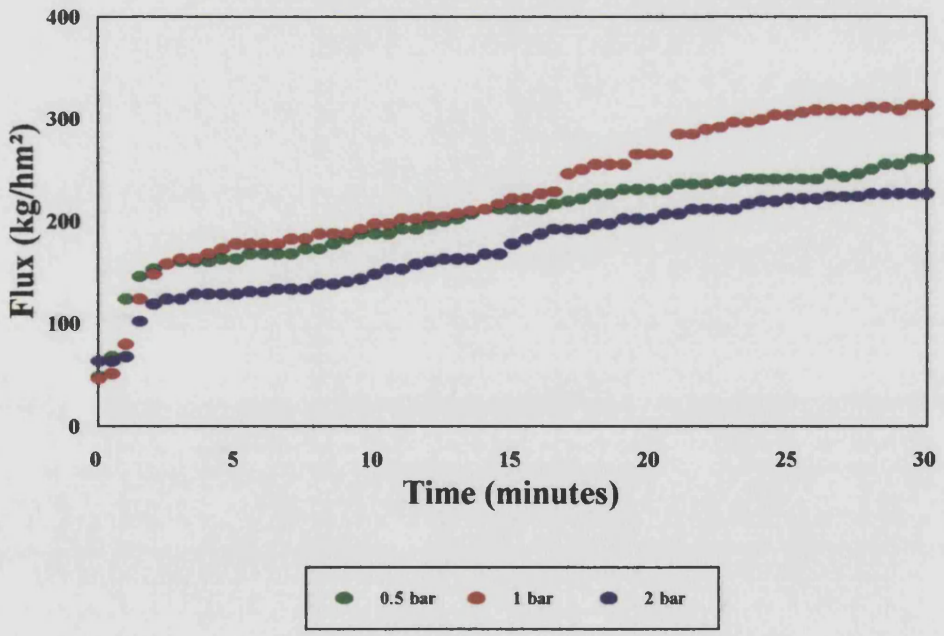



***Figure 4.23b*** *Effect of fouling TMP on flux recovery for a Supor 100 PES membrane cleaned with 0.4 wt.% sodium hydroxide solution at 50°C with a TMP of 0.5 bar and a CFV of 1.59 $ms^{-1}$*

As shown in Figure 4.23b, a sharp increase in flux was observed during the first 2 minutes of the cleaning procedure. This rate of flux recovery, during the first stages of the cleaning procedure, was directly related to the fouling pressure. A fouling TMP of 0.5 bar gave the best rate of recovery. A short lag period was followed by an increase in the cleaning rate for membranes fouled with a 2 bar TMP.

The rate of flux recovery during cleaning can be related to the type of fouling. The removal of surface deposits was easier with membranes fouled using moderate TMP's. Greater pressures during fouling have been shown to decrease the flux recovery rate during the early stages of cleaning. Increased pressure resulted in a more compressed fouling layer, making it more difficult to remove the deposit. The overall flux recovery was again related to the presence and severity of in-pore fouling.

### 4.8.3 Effect of Fouling Crossflow Velocity on Cleanability

Figure 4.24a relates flux decline to CFV in an overlay plot of flux recovery v.'s time for Supor 100 PES membranes fouled with 3.5 wt.% WPC solution at 50°C with a moderate TMP of 1.0 bar.

Higher permeation rates were obtained by increasing the linear velocity for microfiltration. Using a low crossflow velocity of 0.53 $ms^{-1}$ (Re = 1592) resulted in a severely reduced process flux. The fouling rate was rapidly stabilised and a constant flux was observed. With an increased crossflow rate of 1.04 $ms^{-1}$ (Re = 1935), there was an initial increase in the permeation rate which, rapidly declined throughout the fouling period. The fouling profile was of the same form with a CFV of 1.59 $ms^{-1}$ (Re = 4055). However, increasing the CFV from 1.04 $ms^{-1}$ to 1.59 $ms^{-1}$ increased the membrane flux by approximately 30 $kg/hm^2$, for a 53% increase in linear velocity.

A linear velocity of 0.53 $ms^{-1}$ is by definition, 'out of bounds' for true crossflow operation [Coulson and Richardson (1991)]. When using a low crossflow velocity the shear stress effects of the regime appear to be insufficient to overcome accumulation at the membrane surface. Increasing the linear velocity to above 1 $ms^{-1}$ does appear to set a fouling trend, though this does not correspond to the change from a laminar (Re < 2100) to a turbulent (Re > 4000) flow regime.

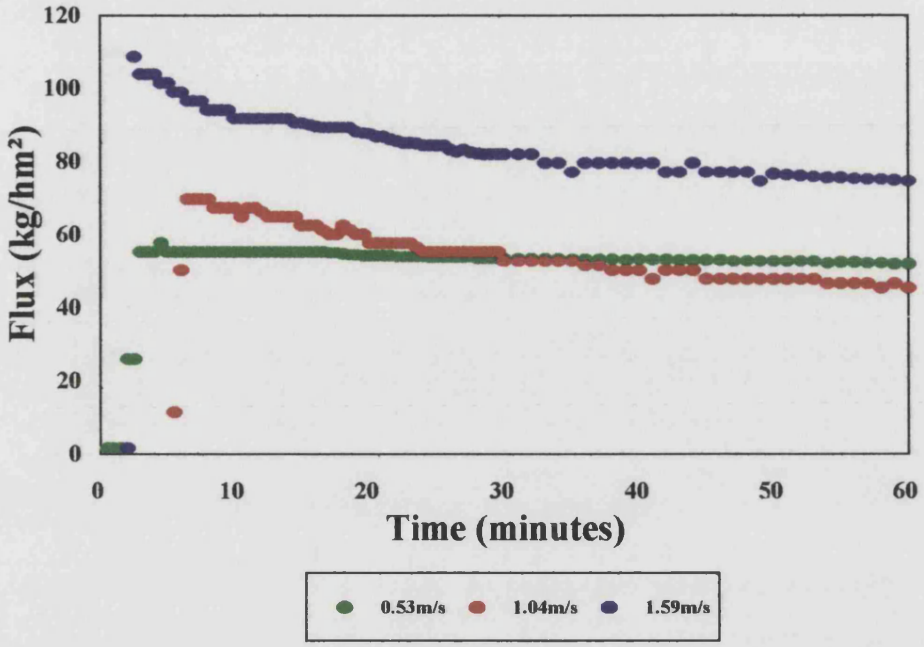



***Figure 4.24a*** *Effect of fouling CFV on flux decline for a Supor 100 PES membrane using a 3.5 wt.% protein solution at 50°C with a TMP of 1.0 bar.*

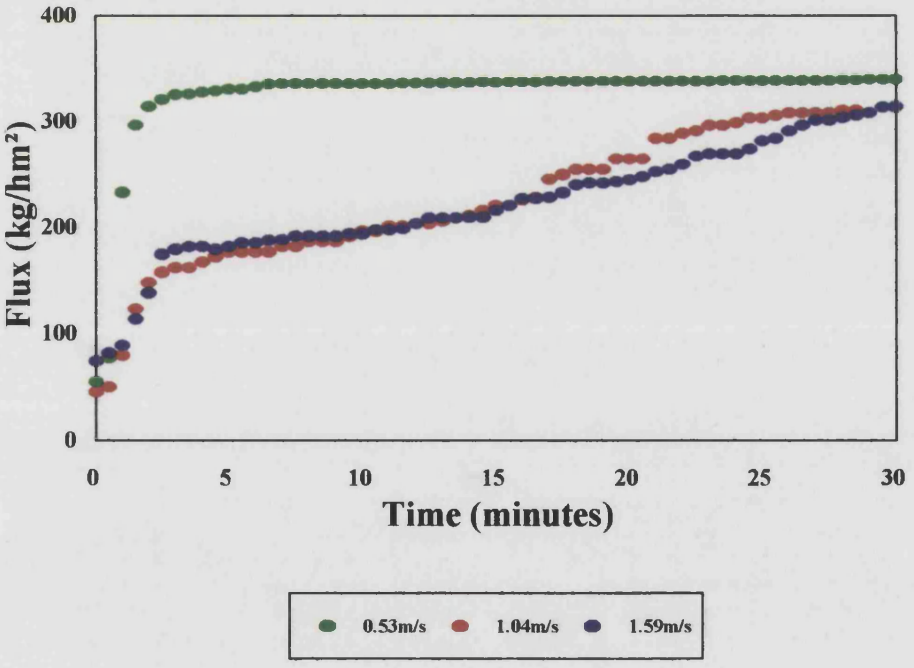



***Figure 4.24b*** *Effect of fouling CFV on flux recovery for a Supor 100 PES membrane using 0.4 wt.% sodium hydroxide solution at 50°C with a TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$.*

Using standard cleaning conditions produced a rapid flux recovery for membranes fouled using the lowest flow conditions (Figure 4.24b). A fouling CFV of 0.53 $ms^{-1}$ resulted in a flux recovery of 71% during the first 2 minutes. Cleaning membranes fouled using higher linear velocities showed almost synchronous flux recovery profiles. A rapid increase in flux during the first 2 minutes resulted in a flux recovery of approximately 35%, with a gradual increase in permeability taking the flux recovery up to 72% after 30 minutes cleaning with sodium hydroxide.

Characterising the removal of in-pore material was the determining factor for flux recovery. The lowest flow conditions resulted in rapid surface fouling, with little in-pore deposition, during the filtration process. This allowed the relatively easy removal of deposit during cleaning with sodium hydroxide. The removal of in-pore material, deposited during the initial stages of fouling with high CFV's, meant a slower flux recovery rate and less complete cleaning operation for the same cleaning time.

## 4.9 MEMBRANE CLEANING MECHANISMS

Through an extensive experimental study, and the visualisation of the cleaning process, it has been possible to identify the key parameters which affect deposit removal, and elucidate the mechanisms of flux recovery.

Whilst the ultimate flux recovery value at the end of the clean is important, characterising the cleaning profile provides the necessary information for optimising the cleaning process. Examination of the typical cleaning profiles shows that flux recovery can be roughly divided into 3 sections (Figure 4.25):

- **Section 1.** Loosely bound material is solubilised on contact with sodium hydroxide. This causes a sharp increase in flux during the first few minutes of cleaning. Examination of the cleaning data shows that the flux recovery rate is dependent on concentration, temperature and crossflow velocity. Transmembrane pressure has little effect on flux recovery in this section.

- **Section 2.** Proteinaceous deposits, which are more tightly bound and present in the pores of the membrane, cannot be readily removed due to the tenacious nature of the material. Caustic cleaning agents are capable of

removing this material. The effectiveness and efficiency of the flux recovery depended primarily on the hydraulic conditions, and to a lesser extent the concentration and temperature.

- **Section 3.** Adsorbed or residual material on the membrane surface and in the pores of the membrane accounts for any losses in the permeability and selectivity of the membrane. Residual material also promotes fouling during the next filtration use. The removal of this material is dependant on the hydraulic conditions and to a lesser extent the solubilisation properties of the cleaning solution.

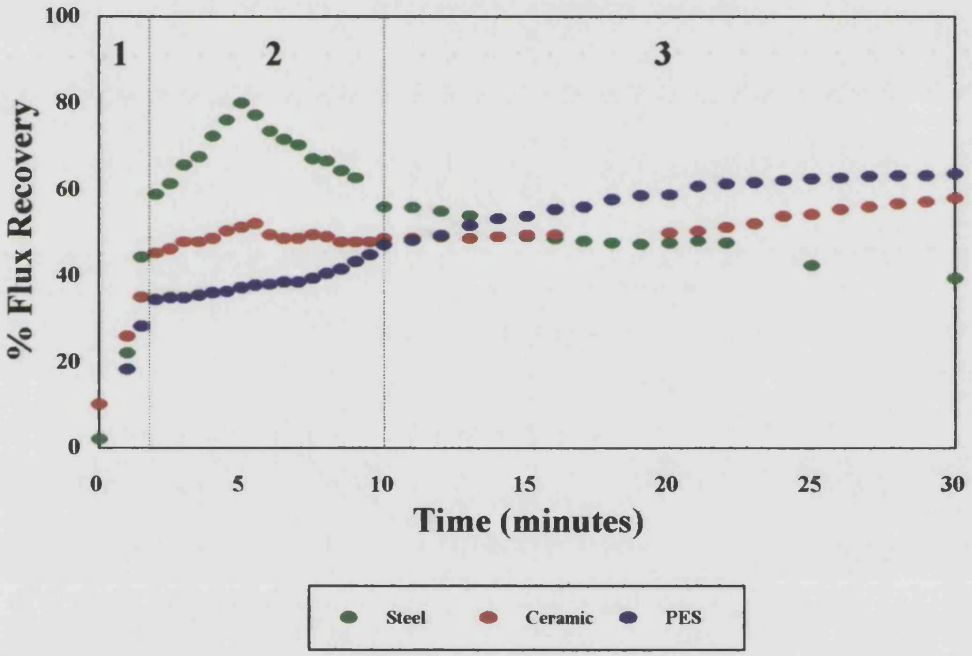



***Figure 4.25*** *Typical flux recovery profiles for the cleaning of sintered stainless steel, ceramic and PES membranes using 0.2 wt.% sodium hydroxide solution at 50℃ with a TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$*

Concentration optima, found when cleaning protein-based deposits from hard surfaces, were explained in terms of the morphological changes the deposit underwent on contact with sodium hydroxide [Bird and Fryer (1992), Bird (1993)]. The swelling

and voidage characteristics of the deposit structure, were important for determining the optimum cleaning conditions. The transfer of this knowledge from hard surfaces to membrane systems is a novel approach that is central to the mechanistic and modelling studies of this project.

Flux recovery, is clearly concentration and temperature dependent. The removal of both surface and in-pore deposits may be explained by morphological changes in the deposit, as well as deposit interactions with the porous membrane structure. The deposit becomes swollen, the swelling increases to a point where the maximum voidage occurs at the optimum concentration. Further increases in concentration lead to a reduction in the deposit voidage.

The optimum sodium hydroxide concentrations found for cleaning membranes with an applied transmembrane pressure (0.2 wt.% for the 2 μm sintered stainless steel membrane, 0.4 wt.% for the 0.1 μm ceramic membrane) were found to differ from those found at zero TMP and for hard surface removal, 0.5 wt.%. The differences in the observed optima are hardly surprising when one considers the structure of the different surfaces.

An optimum temperature of 50°C may also be explained in terms of the structure of the swollen deposit. At low temperatures any increase will aid the cleaning process by speeding up the chemistry of deposit breakdown and decreasing the solution viscosity. High temperatures have been found to produce tenacious deposits, and a high swelling capacity [Bird (1993)], which is not susceptible to breakdown by sodium hydroxide. The inverse solubility of calcium may also reduce the effectiveness or sodium hydroxide cleaning.

As cleaning progresses the surface deposits become highly swollen. The deposit may collapse into the pores of the membrane if the transmembrane pressure compresses the deposit or the crossflow velocity is not sufficient to sweep the layers away. These factors are particularly significant for high flux, large pore microfiltration membranes and may result in a flux decline after the deposit has reached its maximum swelling point.

## 4.10 CONCLUSIONS

Optimisation of the chemical cleaning conditions required the generation of kinetic data. A sufficiently severe and reproducible deposit was required to determine the effectiveness of each cleaning procedure. A fouling protocol was developed to generate sufficiently severe and reproducible fouling deposits for comparative, *in-situ* cleaning experiments. Analysis of the foulants has defined the state of the membrane and the nature of the deposits.

The efficiency of formulated cleaning agents has been studied in comparison with simple cleaning chemicals. In the absence of chemical cleaning agents, flux recovery was poor, as it was with acidic cleaning agents. Caustic based cleaning agents promoted flux recovery and the removal of proteinaceous deposits. The addition of chelating agents to sodium hydroxide improved flux recovery by solubilising minerals. The addition of surfactants showed the potential for increasing solution-deposit contact and preventing the redeposition of deposits. The formulated cleaning agent, Ultrasil 11, gave the highest maximum flux recovery values.

Nitric acid had a detrimental effect on the removal of proteins. Evaluation of multistage regimes revealed that single stage caustic cleaning was more effective for the removal of WPC deposits than multistage alkali/acid sequence cleaning.

A systematic experimental study identified concentration and temperature optima for the cleaning of protein fouled MF membranes by sodium hydroxide. Apparent differences in the flux recovery for the three membrane types tested were explained by changes in the deposit morphology on contact with sodium hydroxide and deposit interactions with the porous membrane structure. The optimum sodium hydroxide concentrations found for cleaning membranes with a positive transmembrane pressure were found to greatly differ from those found at zero TMP and for hard surface removal. 0.2 wt.% sodium hydroxide gave the most effective flux recovery for the 2 μm sintered stainless steel membrane and 0.4 wt.% for the 0.1 μm ceramic membrane. This compared to an optimum sodium hydroxide concentration of 0.5 wt.% for zero TMP flow and hard surface cleaning [Bird and Fryer (1991), Bird (1993)].

It has been commonly suggested that TMP's less than that used for the filtration should be used during cleaning. These results demonstrate that any applied

pressure during cleaning will not result in maximum cleaning efficiency when surface deposits remain. When the surface is free of deposit the removal of in-pore material can be achieved by employing a TMP which is slightly higher than the fouling pressure.

In agreement with several cleaning studies, notably, Hodgson and Fane (1991), Daufin *et al* (1992) and Kim *et al* (1993), no optimal relationship was found for CFV within the scope of this study. However, increasing the cleaning fluid velocity always enhanced the flux recovery. Changes in CFV primarily affect the removal of dissolved material. High CFV's are needed to remove reaction products and prevent redeposition.

In addition to quantitative experiments, information concerning cleaning was obtained by qualitative observation of membrane samples. Visualisation of the cleaning process using SEM and x-ray microanalysis linked flux recovery to deposit removal.

Using PES and ceramic membranes at elevated temperatures, the effects of prolonged contact with water, nitric acid and sodium hydroxide solutions was examined. The results showed that even in this static system moderate cleaning agent concentrations and temperatures caused irreversible damage to the membrane structure. This damage would affect membrane performance and have consequences for the operational lifetime of the membrane.

The study of the permeation characteristics of a PES MF membrane, through multiple cycles, demonstrated that fouling and cleaning procedures could modify the membrane, causing irreversible changes to the structure and chemistry. These changes affected the performance of a membrane and the adsorption of macrosolutes from the solution to the membrane surface. The choice of membrane, and the conditioning and cleaning procedures it undergoes are important, as the initial protein-membrane interactions determine the extent of membrane fouling and, hence, the subsequent permeation characteristics of that membrane.

A preliminary study has shown that membrane cleaning can be characterised in terms of the fouling conditions and the nature of the deposit formed. Generally, increasing the fouling temperature, CFV or TMP resulted in a deposit that was more difficult to remove. The removal of in-pore material was the determining factor for flux recovery and membrane cleanability. Fouling regimes that give high fluxes or increase protein transmission promote in-pore fouling.

Through an extensive experimental study, and visualisation of the cleaning process, it has been possible to identify the key parameters that affect flux recovery. Utilising the knowledge of the swelling and voidage characteristics of proteinaceous deposit structure, determined by hard surface cleaning studies, enabled the mechanisms of flux recovery to be elucidated. Flux recovery and the removal of both surface and in-pore deposits, was explained by morphological changes in the deposit, as well as deposit interactions with the porous membrane structure. We now have a much greater understanding of the mechanisms for the chemical cleaning of MF membranes fouled with whey proteins.

# CHAPTER 5

# MODELLING CLEANING

## 5.0 INTRODUCTION

An extensive, systematic, experimental study has quantified the key parameters for flux recovery and visualisation has made it possible to link the flux recovery process to the removal of deposit with time. As a result, the mechanisms which lead to flux recovery have been postulated (Chapter 4).

As reviewed in Chapter 2, there has been little relevant information published on this area of study and it remains difficult to model experimental data from such complex systems. In developing models to describe the cleaning process it is important to maintain a balance between over-simplification and sophistication. The models described in this chapter are novel and present an approach which is physically realistic.

A qualitative model is presented that describes the flux recovery process in terms of morphological changes to the deposit when it is contacted with chemical cleaning agents.

A mathematical model is proposed which describes the unsteady state hydraulic resistance variation that occurs when cake and in-pore deposition undergo morphological changes during caustic cleaning. The model relies on simultaneous first order swelling and removal processes where unknown parameters are fitted through regression analysis. The reliability and validity of the model are discussed for a single data set using a 2 μm sintered stainless steel membrane. A great deal of future work is required for the model to be accomplished.

## 5.1 QUALITATIVE MODEL DEVELOPMENT

A systematic matrix of curves has been produced for the flux recovery that occurs during the cleaning of inorganic and polymeric MF membranes with sodium hydroxide (Chapter 4). Data has been produced over a concentration range of 0 - 1.0 wt.% sodium hydroxide and a temperature range of 20 - 70°C. The effects of CFV in the

range of 0.26 - 1.90 $ms^{-1}$ and TMP over a range of 0 - 1.0 bar have been quantified.

Figure 5.1 depicts typical flux recovery profiles for a 2 μm sintered stainless steel membrane (Pall Filtration Ltd), a 0.1 μm ceramic membrane (NWW Acumem) and a Supor 100 PES membrane (Gelman Sciences) using 0.2 wt.% sodium hydroxide solution at a temperature of 50°C with a TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$.

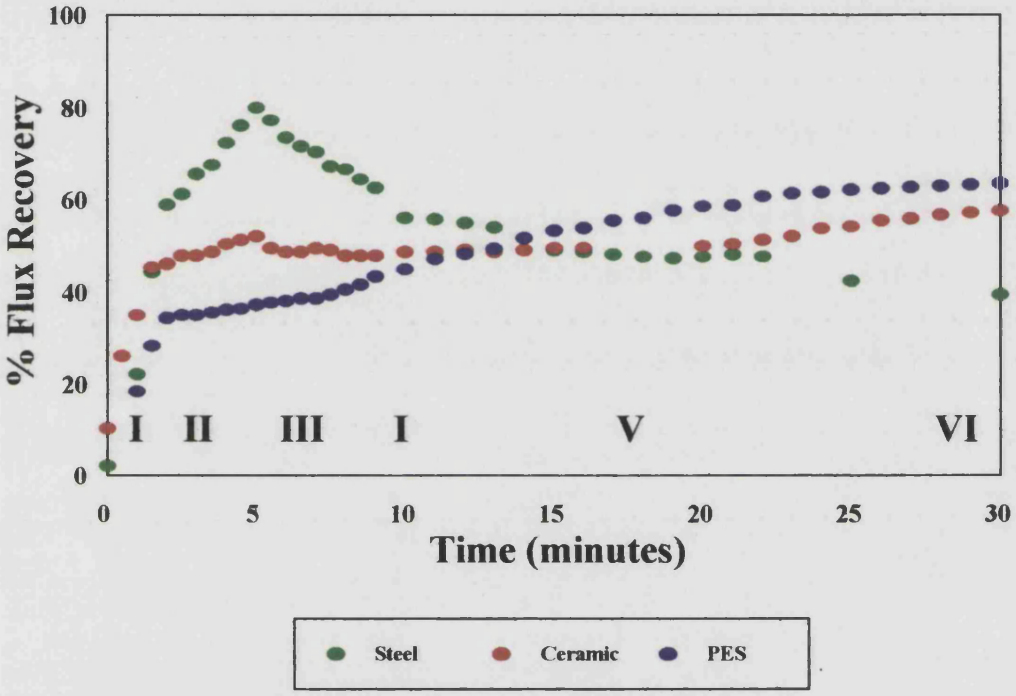



***Figure 5.1*** *Typical flux recovery curves during the cleaning of MF membranes*

Visualisation of the cleaning process has identified that whey protein fouling can be classified as:

**(i)** Loosely bound material

**(ii)** Tenaciously bound material

**(iii)** In-pore material

Thus, a qualitative model, which describes the mechanisms of flux recovery in terms of deposit removal, has been hypothesised. For simplicity, we can consider 6 phases when WPC deposits are contacted with caustic cleaning agents:

(I) **Phase 1** - Rapid removal of loosely bound proteins

(II) **Phase 2** - Swelling of the proteinaceous matrix

(III) **Phase 3** - Removal of proteinaceous matrix

(IV) **Phase 4** - Swelling of in-pore deposition

(V) **Phase 5** - Removal of in-pore deposition

(VI) **Phase 6** - Loss in performance due to residual material

On contact with low concentrations of sodium hydroxide ***loosely bound material*** on the surface of the membrane is easily solubilised. This causes a rapid increase in flux during the first few minutes of the cleaning procedure. **(Phase I)**

Proteinaceous deposits that are more tightly bound or present in the pores of the membrane cannot be readily removed due to their tenacious nature. Chemical cleaning agents are capable of removing this deposit. Morphological changes to the deposit structure, as well as the ***swelling and voidage characteristics*** of the deposit are important in determining the optimum cleaning conditions **(Phases II and IV)**. The effectiveness and efficiency of the flux recovery depend on the cleaning agent used, it's concentration and temperature and the ***operating conditions*** employed **(Phase III and V)**.

***Residual*** (or adsorbed) material on the surface, and in the pores, of the membrane accounts for the loss in permeability and selectivity of the membrane. It also promotes fouling during following operations **(Phase VI)**

In reality, chemical cleaning is complicated, and the mechanisms of removal do not occur sequentially. A multi-layer model is required to accurately depict the simultaneous mechanisms of flux recovery. However, examination of the cleaning data shows us that the final flux recovery is governed by the removal of surface deposits and the swelling of in-pore material.

## 5.2 MATHEMATICAL MODEL DEVELOPMENT

Cleaning is highly complex. The following section represents the first step in the development of a model which characterises membrane cleaning. The essential features of the cleaning process have been represented by a simple model that reflects the events of flux recovery.

### 5.2.1 A Model to Calculate the Resistance to Flow Through Microporous Membranes During Cleaning.

As summarised in Chapter 2, the permeability of MF membranes can be described in terms of the flux, or the resistance to transport, across the membrane:

$$J_v = \frac{TMP}{\mu R_T} \quad \text{or} \quad R_T = \frac{TMP}{\mu J_v} \tag{5.1}$$

Where the total resistance $R_T$, is due to the membrane itself $R_M$, and all the other resistance's arising from the presence of solute.

$$R_T = R_M + R_{cp} + R_F \tag{5.2}$$

The resistance due to concentration polarisation, $R_{cp}$, is removed by the termination of the fouling operation and the release of the applied transmembrane pressure. The resistance due to membrane fouling ($R_F$) can be removed by chemical cleaning.

Ideally, the resistance to permeation will tend to $R_M$ as all the deposit is removed during cleaning (Figure 5.2). Equation 5.3 shows that for a membrane to be clean the resistance due to fouling, $R_F$, must be zero, i.e. the total resistance to permeation, $R_T$ must be equal to $R_M$.

$$R_T \approx R_M \quad \text{at} \quad t=\infty \tag{5.3}$$

Figure 5.3 shows a kinetic profile for a 2 μm sintered stainless steel membrane cleaned using a 0.2 wt.% sodium hydroxide solution at 50°C with a TMP of 0.5 bar and CFV of 1.59 $ms^{-1}$. Resistance plotted against time initially shows an exponential decrease to a minimum value with a gradual increase for the rest of the cleaning period. The cleaning process is clearly complex. The mechanisms imply parallel swelling and removal processes. Thus, for this case, the change in resistance can not be described as a single first or second order kinetic equation as has been suggested by Daufin *et al* (1993).

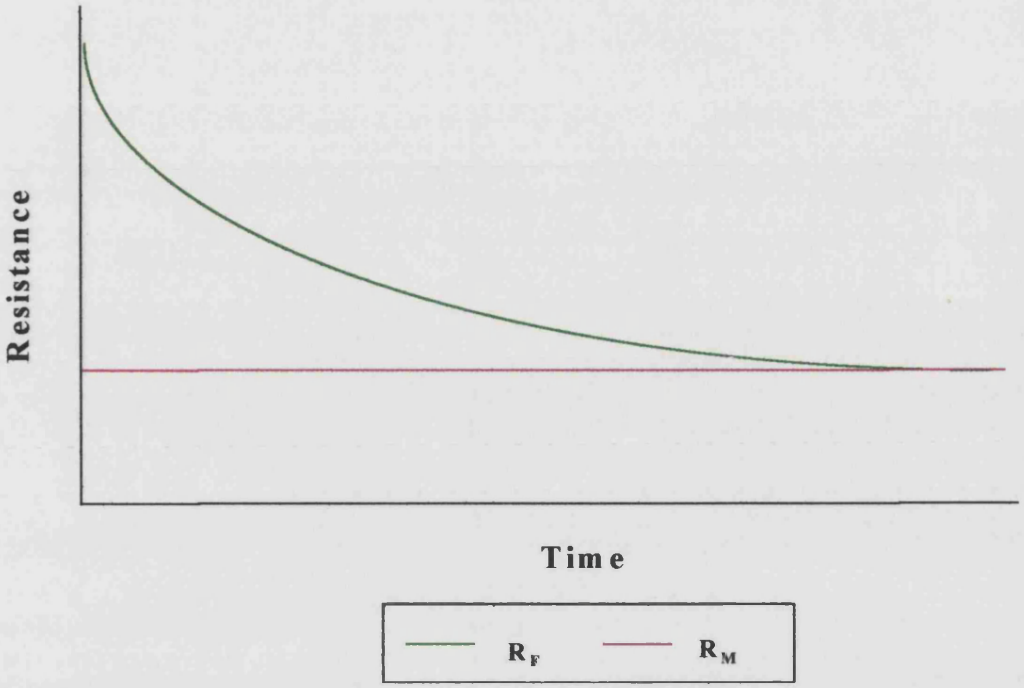



***Figure 5.2*** *Decrease in resistance with time during cleaning*

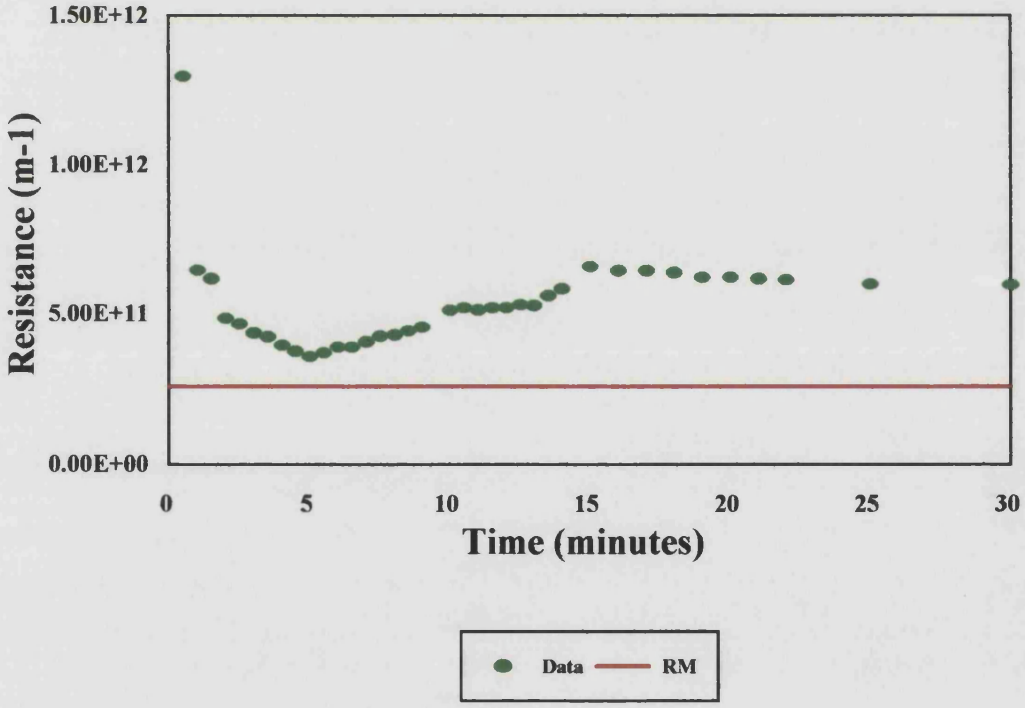



***Figure 5.3*** *Resistance plotted against time for a 2 μm sintered stainless steel membrane cleaned with 0.2 wt.% sodium hydroxide at a temperature of 50°C with a TMP of 0.5 bar and a CFV of 1.59 $ms^{-1}$*

### 5.2.2 Theory

Modelling the resistance during cleaning is kept deliberately simple but reflects the mechanisms described. The proposed model describes the resistance to permeation during cleaning in terms of the unsteady-state change in two hydraulic resistances - the removal resistance and the swelling resistance of the deposit. As a result, the total resistance or flux can be estimated at any time, as:

$$R_T = R_S + R_R + R_M \qquad \textbf{(5.4)}$$

#### *5.2.2.1 Removal Resistance*

The removal resistance $R_R$ is modelled by a simple resistance decrease as the deposit is removed during cleaning (Equation 5.4).

$$\frac{dR_R}{dt} = -k_\alpha R_R \qquad \textbf{(5.5)}$$

Where $R_R$ is dependent on the transmembrane pressure and the viscosity of the cleaning solution, hence the importance of concentration and temperature.

#### *5.2.2.2 Swelling Resistance*

As detailed in Chapter 2 the resistance to flow through a nodular type of membrane, such as the sintered stainless steel membrane, is best described by the equation modified for flow through a granular bed [Carmen-Kozeny (1937)]

$$R = \frac{36h_k(1-\varepsilon)^2 l}{\varepsilon^3 d_e^{\,2}} \qquad \textbf{(5.6)}$$

Analysis of the fouling process (Section 4.1), and examination of the sintered stainless steel membrane surfaces using x-ray microanalysis, suggested that there was a high degree of proteinaceous in-pore fouling. Consequently, the pore bound material will cause a reduction in the original pore diameter, $d_o$. Therefore, the effective pore diameter, $d_e$, is given by:

$$d_e = d_o - 2d_{dep} \tag{5.7}$$

Where $d_{dep}$ is equal to the thickness of the deposit in the pore. Hence,

$$R = \frac{36h_k(1-\varepsilon)^2 l}{\varepsilon^3\left(d_o - 2d_{dep}\right)^2} \tag{5.8}$$

A further reduction in the effective pore diameter occurs when the in-pore deposit swells on contact with sodium hydroxide.

As described in Chapter 2, Bird (1993) presented a kinetic model to describe the diffusion and reaction in a deposit of initial thickness $\delta$, which could be considered as two layers. The upper layer of swollen deposit, which could be removed, had a thickness of $\delta y\chi$. The lower layer of deposit with a thickness of $\delta x$ was not yet removable. $\chi$ is the ratio of swollen to unswollen deposit thickness. This swelling factor $\chi$ was measured visually to be 2.5.

For a swollen deposit of thickness $\delta$

$$d_{dep} = \delta = y\delta\eta + x\delta \tag{5.9}$$

Hence, the resistance due to in-pore swelling, $R_S$, is given as

$$R_S = \frac{36h_k(1-\varepsilon)^2 l}{\varepsilon^3\left(d_o - 2(y\delta\chi + x\delta)\right)^2} \tag{5.10}$$

The resistance is dependent on the porosity ($\varepsilon$), nominal pore size ($d_o$), thickness ($l$) and tortuosity ($h_k$) of the membrane. In addition, the thickness of the protein deposited in the pores and it's swelling characteristics ($\chi$) on contact with sodium hydroxide affect the effective pore diameter.

The equations governing the rate of change in thickness of the deposited layer can be expressed as:

$$\frac{dx\delta}{dt} = -k_\alpha x^n \qquad (5.11)$$

where $y = 1 - x$ (5.12)

### 5.2.3 The Proposed Model

Work to date has shown that a first order removal resistance, working simultaneously with first order in-pore deposit swelling, provided the best data fit.

**For a first order removal resistance**

For a resistance $R_R$

$$\frac{dR_R}{dt} = -k_1 R_R \qquad \textbf{i.e.} \qquad R_R = ke^{-k_1 t} \qquad (5.13)$$

**For a first order swelling resistance**

For a deposit of thickness $x$

$$\frac{dx\delta}{dt} = -k_{P1} x \qquad (5.14)$$

Integration gives

$$x = k_{P2} e^{-k_{P1} t/\delta} \qquad (5.15)$$

when $t=0$ $x=1$

$t=\infty$ $x=0$

Since $y=1-x$ $$y = \left(1 - k_{P2} e^{-k_{P1} t/\delta}\right) \qquad (5.16)$$

For the total deposit thickness

$$d_{dep} = y\delta\chi + x\delta = \delta\chi\left(1 - k_{P2}e^{-k_{P1}t/\delta}\right) + \delta\left(k_{P2}e^{-k_{P1}t/\delta}\right) \quad \textbf{(5.15)}$$

Therefore,
$$d_e = d_o - 2\left[\delta\chi\left(1 - k_{P2}e^{-k_{P1}t/\delta}\right) + \delta k_{P2}e^{-k_{P1}t/\delta}\right] \quad \textbf{(5.16)}$$

Consequently
$$R_S = \frac{36h_k(1-\varepsilon)^2 l}{\varepsilon^3\left(d_0 - 2\left[\delta\chi\left(1 - k_{P2}e^{-k_{P1}t/\delta}\right) + \delta k_{P2}e^{-k_{P1}t/\delta}\right]\right)^2} \quad \textbf{(5.17)}$$

Simulation of the of the model is based on the flux recovery characteristics of 2μm sintered stainless steel membranes fouled using a 3.5 wt.% reconstituted protein solution at 50°C (Figure 5.4).

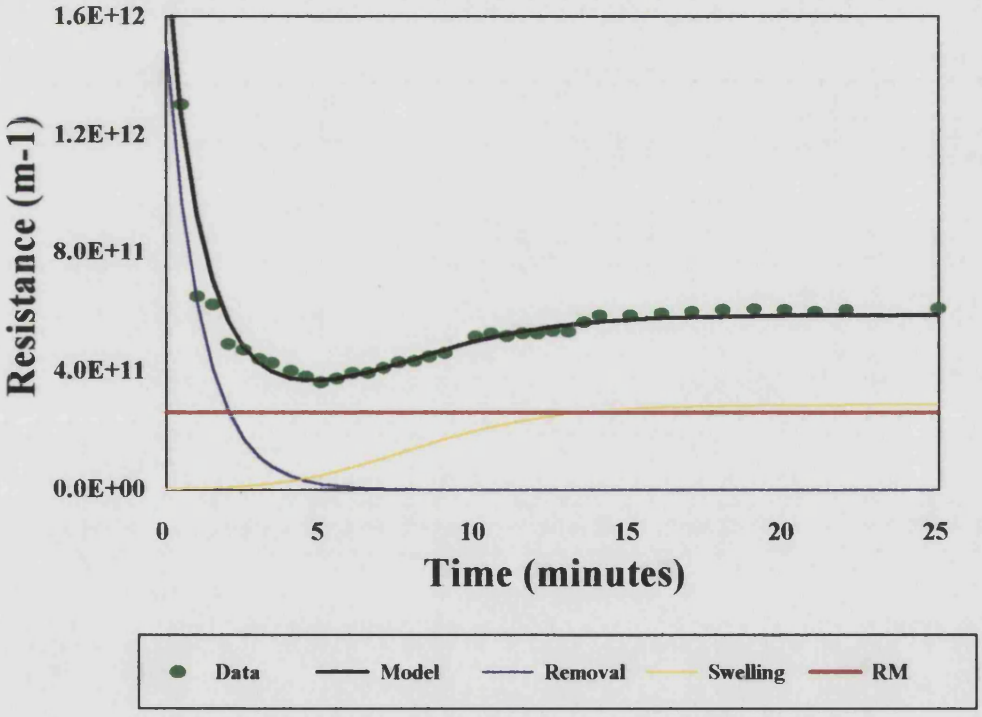



***Figure 5.4*** *Modelling the resistance during cleaning for a 2 μm sintered stainless steel membrane cleaned with 0.2 wt.% sodium hydroxide at 50°C with a TMP of 0.5 bar and a CFV of 1.59 ms$^{-1}$*

The parameters used are given as

| | | |
|---|---|---|
| $R_M = 3 \times 10^{11}$ m$^{-1}$ | $h_K = 5$ | $k = 1.4 \times 10^{12}$ |
| $\varepsilon = 0.25$ | $\chi = 2.5$ | $k_1 = 0.87$ |
| $l = 1 \times 10^{-4}$ m | $\delta = 1 \times 10^{-7}$ m | $k_{P1} = 50$ |
| $d_o = 2 \times 10^{-6}$ m | | $k_{P2} = 3.9 \times 10^{-8}$ |

### 5.2.4 Validity of Model

The strength of the model directly lies in its direct development from experimental observations.

Many parameter values were determined experimentally. The membrane resistance, $R_M$, was determined experimentally at fixed pressure, temperature and crossflow velocity. The porosity ($\varepsilon$), thickness ($l$) and nominal pore size ($d_o$) characteristics of the sintered stainless steel membrane were supplied by the membrane manufacturer. The kozeny factor ($h_k$) was determined experimentally, and found to lie within the recognised limits for inorganic membranes [Benkahla (1993)]. The swelling factor ($\chi$) was determined through visual observation of WPC swelling characteristics on hard surfaces [Bird (1993)].

The thickness of the in-pore deposit ($\delta$) has been selected to lie within its recognised value range. Only the four rate constants ($k$, $k_1$, $k_{P1}$ *and* $k_{P2}$) are fully adjustable and can be chosen to provide the best fit to data.

Whilst the simulation shows a good fit to the experimental data, sensitivity analysis is required to determine the relative importance of the adjustable parameters. Analysis in the variation of these adjustable parameters, as a function of the cleaning agent concentration and thermo-hydraulic conditions, also needs to be investigated.

The fitting of the full range of experimental results is required to determine the true usefulness of current model.

## 5.3 CONCLUSIONS

A qualitative model is presented that describes the flux recovery process in terms of morphological changes to the deposit on contact with chemical cleaning agents.

A mathematical model is proposed which describes the unsteady state hydraulic resistance variation that occurs when cake and in-pore deposition undergo morphological changes during caustic cleaning. The model relies on simultaneous first order swelling and removal processes where unknown parameters are fitted through regression analysis of experimental results.

Whilst the simulation shows a good fit to the experimental data the relative importance and variation of the adjustable parameters needs to be determined.

The application of the model is discussed along with possible future modelling developments in Chapter 6.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6.0 INTRODUCTION

The cleaning of membranes fouled with proteins is complex. Current cleaning practices have been established on a practical basis, which has provided little information on the fundamental mechanisms involved.

Through an extensive, systematic experimental study the key cleaning compounds for the removal of proteinaceous deposits have been identified and examined. A much greater understanding of the mechanisms for the chemical cleaning of flat-sheet MF membranes has been gained.

The discovery of optimum values for cleaning agent concentration and temperature, and the evaluation of the operating conditions that maximise flux recovery, means that cleaning conditions can be selected to minimise chemical consumption.

Qualitative and mathematical membrane cleaning models have been developed which describe flux recovery well.

## 6.1 EXPERIMENTAL SYSTEM

An experimental apparatus has been designed and constructed to generate fouled membrane systems, and then clean them, *in-situ* under controlled thermo-hydraulic conditions. The cleaning and fouling rig incorporates a stainless steel module, designed to house any flat sheet membrane. Replaceable perspex inserts allowed channel geometry, and hence, crossflow to be controlled.

Flux recovery was used as the main criteria for the quantitative assessment of cleaning efficiency, while HPLC was employed to evaluate changes in permeate quality. Visual examination, Scanning Electron Microscopy and x-ray microanalysis provided a more detailed appraisal of the membrane state, and were used to relate deposit removal to the cleaning kinetics.

## 6.2 EXPERIMENTAL RESULTS

A fouling protocol was developed to generate sufficiently severe and reproducible whey protein deposits for comparative cleaning experiments. Analysis of the foulants on sintered stainless steel, ceramic and polyethersulphone microfiltration membranes defined the state of the membrane and the nature of the deposits.

An extensive, experimental study was carried out for single and multistage cleaning regimes, using both simple and formulated cleaning agents. The key cleaning compounds for the removal of proteinaceous deposits have been identified and the operating parameters examined.

Systematic cleaning experiments with sodium hydroxide identified concentration and temperature optima that maximised flux recovery. Using cleaning conditions above the optima reduced cleaning efficiency.

No optimal relationship was found for CFV within the scope of this study. However, increasing the cleaning fluid velocity always enhanced the flux recovery. This indicates that changes in CFV primarily affected the removal of dissolved material.

Any applied TMP, during cleaning, was found to reduce cleaning efficiency. Flux recovery was less dependent on the surface characteristics of the membrane with decreasing TMP

Dynamic studies have shown that the subsequent permeation characteristics of membranes were dependent on the conditioning and cleaning procedures applied to them. Static experiments showed that even moderate cleaning agent concentrations and temperatures caused irreversible damage to the membrane structure, with severe implications for the operational life of membranes.

It has been shown that cleaning can be characterised in terms of the fouling conditions and the nature of the deposit. Fouling conditions that gave high process fluxes or increased protein transmission promoted in-pore fouling, and the membranes were more difficult to clean.

Flux recovery and the removal of deposits, was explained in terms of changes in the deposit morphology, and deposit interactions with the porous membrane structure.

## 6.3 MODEL DEVELOPMENT

A qualitative model has been presented that describes the flux recovery process in terms of morphological changes to deposit contacted with chemical cleaning agents.

A mathematical model has been proposed which was directly developed from experimental observations. The model relies on simultaneous first order swelling and removal kinetics. Many of the parameters were determined experimentally, while others could be selected to lie within their recognised value range. Only the rate constants were fully adjustable and could be chosen to provide the best fit to data.

## 6.4 FUTURE WORK

The results described in this thesis have raised several questions which should be answered and opened-up a wide range of opportunities for future work.

### 6.4.1 The Membrane

A vast array of membrane materials are available, many with specific applications and performance criteria. For the purposes of this study, three types of microfiltration membrane were utilised, with the aim of being representative of the diverse material and structural properties available. The present study should be extended to include ultrafiltration membranes. These membranes are heavily utilised in the separation of complex bio-products, and consequently, suffer severe fouling.

All the experiments in this thesis were carried out in a flat-sheet membrane system. A comparison of cleaning protocols with different module configurations is needed if general cleaning strategies are to be developed. The use of ceramic tubular and spiral wound polymeric membranes are of particular interest within the food and water treatment areas.

### 6.4.2 The Deposit

A reduction in membrane performance due to fouling is an important issue not only in the food but in the biotechnology and waste treatment industries also.

The existence of temperature and cleaning agent optima have been identified for the removal of carbohydrate deposits [Din and Bird (1997)] and crude oil films [Espig (1997)] from hard surfaces. As with the removal of dairy deposits [Bird

(1993)], the transfer of knowledge from these systems could be made to membrane systems. Using the experimental protocols developed in this study, the removal of non-protein deposits from fouled membrane systems could then be optimised.

### 6.4.3 Performance Indicators

Permeate flux is typically used to as the main criterion for assessing both fouling and cleaning behaviour. While a low permeate flux indicates the presence of deposit the converse is not necessarily true. Restoration of flux does not indicate that the membrane system is free of foulants. It is important to select indicators that accurately reflect the complete or thorough cleaning of the system.

Deposit removal has to be related to cleaning kinetics to give a better assessment of the membrane surface. The hydraulic properties of the membrane can be related to the structure and composition of fouling layers by the use of spectroscopic analysis (IR and XPS) and porometry measurements. However, these techniques are invasive by nature and as such are not applicable in industrial environments. Quantitative analysis of retentate and permeate streams, would allow a mass balance of foulants to be determined. Techniques such as UV absorption, colourimetric assays and atomic adsorption allow on line analysis of solutions.

### 6.4.4 Cleaning Experiments

#### *6.4.4.1 Comparative Testing of Cleaning Agents*

An extensive, systematic, study has identified the individual effects of concentration, temperature, flow and transmembrane pressure on flux recovery for caustic cleaning, but none of the test protocols in this study achieved full flux recovery.

The protocols developed could be used to explore the effect of alternative cleaning agents. Nitric acid is widely used in the cleaning of dairy deposits, though the mechanisms of deposit removal are not well understood, or documented. A systematic study would elucidate the mechanisms, thus, aiding the optimisation of two stage cleaning processes.

A study into the synergistic effect of simple cleaning agents, in series or as mixtures would optimise cleaning performance and lead to more responsive cleaning protocols, by improving flux and decreasing cleaning times.

#### 6.4.4.2 *Contribution of the Chemical, Thermal and Hydraulic Cleaning Conditions*

A multi-level examination needs to be conducted to look at the compound effects of the key process parameters. The use of a fractional factorial design would allow the examination of multi-layer experiments, to optimise flux recovery within this system.

While some studies [Nystrom and Zhu (1996)] have assessed the chemical and physical changes that occur with short term membrane use there is little quantitative study on the progressive damage caused by multiple fouling and cleaning studies. This is an area which has vast implications for industrial membrane use and requires immediate attention.

#### 6.4.4.3 *Mechanisms*

The existence of concentration optima appears to be a chemical phenomenon. While proteins are known to swell on contact with caustic and acidic solutions to produce a gel like material, the biochemistry of the process is not well understood for the extremes of pH used in aggressive chemical cleaning regimes. Further knowledge and modelling of the gelation and swelling characteristics would be of benefit to mechanistic cleaning studies.

### 6.4.5 Model Development

The modelling approach adopted in this thesis is a first step during the authors PhD's studies. A great deal of future work and validation of the parameters is needed for the model to be accomplished. Fitting the full range of experimental data is required to determine the usefulness of the current model. Sensitivity analysis is required to determine the relative importance of the adjustable parameters. Analysis of these parameters as a function of the cleaning agent concentration and thermo-hydraulic conditions needs to be investigated.

A very simple relationship has been used to describe the resistance during cleaning. A more sophisticated approach could be taken by assuming the cake to be 3-D porous structure. Accurate measurement of the cake parameters would allow the swelling and dissolution kinetics to be incorporated into the model.

The current model could be applied to other nodular membranes, for which a large base of cleaning data has been collected. In addition, the model could be modified for application to other porous systems such as chromatography.

# REFERENCES


**Akay G and Wakeman RJ (1995)**, 'Ultrafiltration and microfiltration of surfactant dispersions - An evaluation of published research', *Trans IChemE*, 71, 411-420.

**Armishaw RF (1982)**, 'Inorganic fouling of membranes during ultrafiltration of casein whey', *NZ Journal f Dairy Science and Technology*, **17**, 213-228.

**Aimar P (1993)**, 'Separation by membranes', *Membranes in Bioprocessing - Theory and Applications*', eds. Howell JA, Sanchez V and Field RW, Blackie Academic Press, Cambridge, UK, **Ch 4**, 113-140

**Attia H, Benasar M and De La Fuente BT (1991)**, 'Study of the fouling of inorganic membranes by acidified milks using scanning electron microscopy and electrophoresis: I. Membrane with pore diameter 0.2 microns', *Journal of Dairy Research*, **58**, 39-50.

**Baird A (1993)**, NWW Acumem, *Personal Communications.*

**Bartlett M (1996)**, *Internal Report*, Laboratoire de Genie Chimique, Universite Paul Sabatier, Toulouse, France.

**Bauser H, Chmiel H, Stroh N, Walitza E (1982)**, 'Interfacial effects with microfiltration membranes', *Journal of Membrane Science*, 321-337.

**Bauser H, Chmiel H, Stroh N, Walitza E (1986)**, 'Control of concentration polarisation and fouling of membranes in medical, food and biotechnological applications', *Journal of Membrane Science*, **24**, 195-202.

**Belfort, G (1977)**, 'Pre-treatment and cleaning of hyperfiltration (reverse osmosis) membranes in municipal waste water renovation', *Desalination*, **21**, 285-297.

**Belfort G (1989)**, 'Fluid mechanics in membrane filtration: Recent developments', *Journal of Membrane Science*, **40**, 123-147.

**Bellara SR, Cui ZF and Pepper DS (1996)**, 'Flux enhancement in hollow fibre membrane systems', *IChemE Research Event*, University of Leeds, Leeds, UK, **I**, 310-312.

**Benkahla YK (1993)**, 'Etude des mechanisms de colmatage et decolmatage d'une membrane minerale en microfiltration', *Ph.D Thesis*, Universite de Technologie de Compiegne, Compiegne, France.

**Bigalke DL (1985)**, 'Effective process monitoring of microbial contamination of dairy products', *Fouling and Cleaning in Food Processing*, eds. Lund DB, Plett E and Sandu C, University of Wisconsin-Madison Extension Duplicating, Madison, USA, 286-311.

**Bird MR and Fryer PJ (1991)**, 'An experimental study of the cleaning of surfaces fouled by whey proteins' *Trans IChemE*, **69**, 13-21.

**Bird MR and Fryer PJ (1992)**, 'An analytical model for the cleaning of food process plant', *IChemE Research Event Book*, 325-331.

**Bird MR (1993)**, 'Cleaning of food process plant', *Ph.D Thesis*, University of Cambridge, Cambridge, UK.

**Bohner HF and Bradley RL (1992)**, 'Effective cleaning and sanitising of polysulphone ultrafiltration membranes', *Journal of Dairy Science*, **75**, 718-724.

**Bourne MC and Jennings WG (1961)**, 'Some physio-chemical relationships in cleaning hard surfaces', *Food Technology*, **15**, 495-499.

**Bowen WR, Kingdon RS and Subuni HAM (1989)**, 'Electrically enhanced separation processes: The basis of *in-situ* intermittent electrolytic membrane cleaning (IIEMC) and *in-situ* electrolytic membrane restoration (IEMR)', *Journal of Membrane Science*, **40**, 219 -229.

**Bowen RW, Calvo JI and Hernández A (1995)**, 'Steps of membrane blocking in flux decline during protein filtration', *Journal of Membrane Science*, **101**, 153-165.

**Brink LES, Elbers SJG, Robbertsen T and Both P (1993)**, 'The anti-fouling action of polymers preadsorbed on ultrafiltration and microfiltration membranes', *Journal of Membrane Science*, **76**, 281-291.

**Broom GP, Squires RC, Simpson MPJ and Martin I (1994)**, 'The treatment of heavy metal effluents by crossflow microfiltration, *Journal of Membrane Science*, **87**, 219-230.

**BS 733 (1987)**, Pyknometers, Parts 1-2.

**BS 188 (1977)**, Methods for determination of the viscosity of liquids.

**Buckley CA, Treffry-Goatley K, Simpson MJ, Bindoff AL and Groves GR (1985)** 'Reverse osmosis and ultrafiltration', ed. Sourirajan, S, 429-437.

**Burton H (1967)**, 'Seasonal variation in deposit formation from whole milk on a heated surface', *Journal of Dairy Research*, **34**, 137-143.

**Carmen PL (1937)**, 'Fluid flow through granular beds', *Trans IChemE*, **15**, 150-166.

**Carver A (1993)**, School of Chemistry, University of Bath, *Personal Communications.*

**Chen V, Fane AG and Fell CJD (1992)**, 'The use of anionic surfactants for reducing fouling of ultrafiltration membranes: Their effects and optimisation', *Journal of Membrane Science*, **67**, 249-261.

**Cheryan M and Merin U (1981)**, 'The effect of protein-mineral-membrane interactions on the fouling of ultrafiltration membranes', *Fundamentals and Applications of Surface Phenomenon Associated with Fouling and Cleaning in Food Processing*, eds. Hallstrom B, Lund DB and Tragardh C, Lund University Press, Sweden, 204-214.

**Cheryan M (1986)**, *Ultrafiltration Handbook*, Technomic Publishing Co., Pennsylvania, USA.

**Chong R, Jelen P and Wong W (1985)**, 'The effective cleaning agents on a non-cellulosic ultrafiltration membrane', *Separation Science and Technology*, **20**, 393- 402.

**Colman DA and Mitchel WS (1991)**, 'Enhanced mass transfer for membrane processes', *Trans IChemE*, **69**, 91-96.

**Coolbear T, Monk C, Peek K, Morgan HW and Daniel RM (1992)**, 'Laboratory scale investigations into the use of extremely thermophilic proteases for cleaning ultrafiltration membranes fouled during whey processing', *Journal of Membrane Science*, **67**, 93-101.

**Coulson JM and Richardson JF (1991)**, *Chemical Engineering*, 4th edition, **VOL. 2,** Pegammon Press, Oxford, UK.

**Coultate, TP (1992)**, *Food: The Chemistry of its Components*, Royal Society of Chemistry, London, UK, 85-105.

**Crane A (1992)**, Pall Filtration Ltd, *Personal Communications.*

**Da Costa AR, Fane AG and Wiley DE (1993),** 'Ultrafiltration of whey protein solutions in Spacer-Filled Flat Channels' *Journal Membrane Science*, **76**, 245-254.

**Daufin G, Labbé JP, Quémerais A, Michel F, Robert F and Fiaud C (1989)**, 'Spectroscopic analysis of fouling layers of inorganic ultrafiltration membranes', *Fouling and Cleaning in Food Processing*, eds. Kessler HG and Lund DB, Munich, FRG, 207-215.

**Daufin G, Merin U, Labbé JP, Quémerais A and Kerherve FL (1991)**, 'Cleaning of inorganic membranes after whey and milk ultrafiltration', *Biotechnology and Bioengineering*, **38**, 82-89

**Daufin G, Merin U, Kerherve FL, Labbé JP, Quémerais A and Bousse C (1992)**, 'Efficiency of cleaning agents for an inorganic membrane after milk ultrafiltration', *Journal of Dairy Research*, **59**, 39-47.

**Daufin G, Michel F, Labbé JP, Quémerais A and Grangeon A (1993)**, 'Ultrafiltration of defatted whey: Improving performance by limiting membrane fouling', *Journal of Dairy Research*, **60**, 79-88.

**Din R and Bird MR (1997)**, 'The removal of starch residues formed during baking by the use of aqueous chemical cleaners', *International Conference on Engineering and Food (ICEF) 7*, Holland, 3-5th April , 33-36.

**Drioli E (1986)**, 'Membranes and membrane processes in biotechnology', *Synthetic Membranes: Science Engineering and Applications*, ed. Bungay PM, 667-682.

**Durham RJ and Nguyen (1994)**, 'Hydrophobic membrane evaluation and cleaning for osmotic distillation of tomato puree', *Journal of Membrane Science*, **87**, 181-189.

**Espig S (1997)**, 'Removal of crude oil films by aqueous detergents', *Ph.D Thesis*, University of Bath, Bath, UK.

**Eykamp W (1995)**, 'Microfiltration and ultrafiltration'. *Membrane Separation Technology: Principles and Applications*, eds. Noble RD and Stern SA, Elsevier Science BV, Amsterdam, Holland, **Ch I**, 1-43.

**Fane A G (1995)**, *Personal Communications.*

**Fick A (1855)**, 'Uber diffusion', *Pogg. Ann.*, **94**, 59-86.

**Field RW, Wu D, Howell JA and Gupta BB (1995)**, 'Critical flux concept for microfiltration fouling', *Journal of Membrane Science*, **100**, 259-272.

**Gallot-Lavalle T and Lalande M (1985)**, 'A mechanistic approach to pasteurised milk deposit cleaning', *Fouling and Cleaning in Food Processing*, eds. Lund

DB, Plett E and Sandu C, University of Wisconsin-Madison Extension Duplicating, Madison, USA, 374-394.

**Gan Q (1992)**, 'Membranes, proteins and microfiltration processes', *Ph.D Thesis*, University College Swansea, Swansea, UK.

**Gan Q and Howell JA (1994)**, 'Fouling and backflush in beer clarification using ceramic membranes', *4th Bath Food Engineering Conference*, University of Bath, Bath, UK.

**Gan Q, Howell JA, Field RW, England R, Bird MR and McKechinie MT (1998)**, 'Synergetic cleaners for a ceramic membrane fouled by beer microfiltration', *accepted by the Journal of Membrane Science.*

**Gésan G, Daufin G, Merin U, Labbé JP and Quémerais (1993)**, 'Fouling during constant flux crossflow microfiltration of pre-treated whey. Influence of transmembrane pressure gradient', *Journal of Membrane Science*, **80**, 131-145

**Giese JH (1991)**, 'Sanitation: The key to food safety and public health', *Food Technology*, **45**, 74-80.

**Glemenius R (1980)**, 'Membrane processes for water, pulp and paper, food: State of the art', *Desalination*, **35**, 259-272.

**Grace HP (1956)**, 'Structure and performance of filter media', *Journal of AIChE.*, **2**, 307-313.

**Grashoff A (1989)**, 'Environmental aspects of the use of alkaline cleaning solutions', *Fouling and Cleaning in Food Processing*, eds. Kessler HG and Lund DB, Munich, FRG, 107 -114.

**Harper WJ and Moody ME (1981)**, 'Enzymatic cleaning of cellulose acetate membrane reverse osmosis systems', *Journal of Food Protection*, **44**, 337-340.

**Heinemann P, Howell, JA and Bryan RA (1988)**, 'Microfiltration of protein solutions: effect of fouling on rejection', *Desalination*, **68**, 243-250.

**Hermia J (1982)**, 'Constant pressure blocking filtration laws - application to power law non-Newtonian fluids', *Trans IChemE*, **60**, 183-187.

**Hodgson PH and Fane AG (1991)**, "Crossflow microfiltration of biomass with inorganic membranes: The influence of membrane surface and fouling dynamics", *Key Engineering Materials*, **61&62**, 167-174.

**Howell JA and Finnegan SM (1991)**, 'Hydrodynamics and membrane filtration', *Effective Industrial Membrane Processes - Benefits and Opportunities*, ed. MK Turner, Elsevier Applied Science, 49-60.

**Jacobs EP, Swart P, Brouckaert CJ and Hart OO (1993),** 'Membrane performance restoration. 1: Abattoir process streams, cleaning regimes for UF membranes', *Waters SA*, **19**, 127-132.

**Jennings WG (1965)**, 'Theory and practice of hard surface cleaning', *Advances in Food Research*, **14**, 325-458.

**Kane DR and Middlemiss NE (1985)**, 'Cleaning chemicals - State of the knowledge in 1985', *Fouling and Cleaning in Food Processing*, eds. Lund DB, Plett E and Sandu C, University of Wisconsin-Madison Extension Duplicating, Madison, USA, 312-335.

**Kim KJ, Fane AG, Fell CJD and Joy DC (1992)**, 'Fouling mechanisms of membranes during protein ultrafiltration', *Journal of Membrane Science*, **68**, 79-91.

**Kim KJ, Sun P, Chen V, Wiley DE and Fane AG (1993)**, 'The cleaning of ultrafiltration membranes fouled by protein', *Journal of Membrane Science*, **80**, 241-249.

**Kulozik UM and Kessler HG (1989)**, 'Rinsing behaviour of deposited layers in reverse osmosis and ultrafiltration', *Fouling and Cleaning in Food Processing*, eds. Kessler HG and Lund DB, Munich, FRG, 248-257.

**Labbé JP, Quémerais A, Michel F and Daufin G (1990)**, 'Fouling of inorganic membranes during whey ultrafiltration: Analytical methodology' *Journal of Membrane Science*, **51**, 293-307.

**Lahiere RJ and Goodboy KP (1993)**, 'Ceramic membrane treatment of petrochemical waste water', *Environmental Progress*, **12**, 86-96.

**Le MS (1982)**, 'Membrane ultrafiltration fouling and treatment', *Ph.D Thesis*, University College Swansea, Swansea, UK.

**Le MS and Howell JA (1983)**, 'A model for the effects of adsorbents and cleaners on UF membrane structure', *Chemical Engineering Research and Design*, **61**, 191-198.

**Le MS and Howell JA (1985)**, 'Ultrafiltration', *Comprehensive Biotechnology*, ed. Moo-Young M, Pegammon Press, Oxford, 383-409.

**Leaver G and Melling J (1987)**, 'Cleaning technology for synthetic membranes', *BioSep Biotechnological Separations Club*.

**Lee DN and Merson RL (1975)**, 'Examination of cottage cheese whey proteins by scanning electron microscopy: Relationship to membrane fouling during ultrafiltration', *Journal of Dairy Science*, **58**, 1423-1431.

**Lee S, Ourelle Y and Roques H (1984)**, 'Concentration polarisation membrane fouling and cleaning in ultrafiltration of soluble oil', *Journal of Membrane Science*, **19**, 23-38.

**Lindau J and Jonsson AS (1994)**, 'Cleaning of ultrafiltration membranes after treatment of oily waste water', *Journal of Membrane Science*, **87**, 71-79.

**Lowe E and Durkee EL (1971)**, 'Dynamic turbulence promotion in reverse osmosis processing of liquid foods', *Journal of Dairy Science*, **36**, 31-38.

**Luss G (1984)**, 'Fouling and cleaning in membrane processes involved in dairy applications', *1984 Whey Products Conference*, Chicago, USA.

**Luss G (1985)**, 'Membrane Fouling - Field experience and observations', *Fouling and Cleaning in Food Processing*, eds. Lund DB, Plett P and Sandu C, University of Wisconsin, Madison, USA, 502-515.

**Mackley MR and Sherman NE (1993)**, 'Cake filtration mechanisms in steady and unsteady flows', *Journal of Membrane Science*, 77, 113-121.

**Mehra RK and Donnelly WJ (1993)**, 'Fractionation of whey protein components through large pore size, hydrophilic, cellulose membrane', *Journal of Dairy Research*, **60**, 89-97.

**Merin U and Daufin G (1990)**, 'Crossflow microfiltration in the dairy industry', *Le Lait*, **70**, 281-291.

**Millipore (1994)**, MemSep Chromatography Cartridges Application Note.

**Mulder M (1991)**, *Basic Principles of Membrane Technology*, Kluwier Academic Publishers, London, UK.

**Nakanishi K and Kessler HG (1985)**, 'Rinsing behaviour of deposited layers formed on membranes in ultrafiltration', *Journal of Food Science*, **50**, 1726-1732.

**Nilsson JL (1988)**, 'Fouling of an ultrafiltration membrane by a dissolved whey protein concentrate and some whey proteins', *Journal of Membrane Science*, **36**, 147- 160.

**Nisbet TJ, Thorn TM and Wood PW (1981)**, 'Observations on the fouling of polysulphone ultrafiltration membranes by acid whey', *NZ Journal of Dairy Science and Technology*, **16**, 113-120

**Nystrom M and Zhu H (1996)**, 'Characterisation of cleaning results using combined flux and streaming potential methods', *Journal of Membrane Science*, **131**, 195-205.

**Padilla-Zakour O, and McLellan MR (1993)**, 'Optimisation and modelling of apple juice crossflow microfiltration', *Journal of Food Science*, **58**, 369-374.

**Parkin MF and Marshall KR (1976)**, 'The cleaning of tubular cellulose acetate ultrafiltration membranes', *NZ Journal of Dairy Science and Technology*, **11**, 107-114.

**Perlat MN (1986)**, 'Etude du nettoyage des exchangers a plaques destines a la pasteurisation et a la sterilisation a ultra haute temperature du lait', *Ph.D Thesis*, UST 1 Lille, Lille, France.

**Perry RH and Green D (1992)**, *Chemical Engineers Handbook*, McGraw Hill Publishing, New York, USA, **17**(14-33).

**Plett EA (1985)**, 'Cleaning of fouled surfaces', *Fouling and Cleaning in Food Processing*, eds. Lund DB, Plett E and Sandu C, University of Wisconsin-Madison Extension Duplicating, Madison, USA, 286-311.

**Plett (1985b)**, 'Relevant mass transfer mechanisms during rinsing', *Fouling and Cleaning in Food Processing*, eds. Lund DB, Plett E and Sandu C, University of Wisconsin-Madison Extension Duplicating, Madison, USA, 393-409.

**Razavi SKS, Harris JL and Sherkat F (1996)**, 'Fouling and cleaning of membranes in the ultrafiltration of the aqueous extract of soy flour', *Journal of Membrane Science*, **114**, 93-104.

**Ridgeway HF, Kelly A, Justice C and Olson BH (1983)**, 'Microbial fouling of reverse osmosis membranes used in advanced wastewater treatment technology: Chemical, bacteriological and ultrastructural analyses', *Applied and Environmental Microbiology*, **45**, 1066-1084.

**Robinson CW, Siegel MH, Condemine A, Fee, C, Fahidy, TZ and Glick BR (1993),** 'Pulsed-electric-field crossflow ultrafiltration of bovine serum albumin', *Journal of Membrane Science*, **80**, 209-220.

**Rogers VGJ and Sparks RE (1991),** 'Reduction of membrane fouling in protein ultrafiltration', *Journal of AIChE.*, **37**, 1517.

**Rogers VGJ and Sparks RE (1992),** 'Effect of transmembrane pressure pulsing on concentration polarisation', *Journal of Membrane Science*, 68, 149-168.

**Romney AJD (1990),** *C.I.P: Cleaning in Place*, 2nd Edition, Society of Dairy Technology.

**Rosenberg M (1995),** 'Current and future applications for membrane processes in the dairy industry', *Trends in Food Science and Technology*, **6**, 12-19.

**Satoh S and Nakano H (1995),** 'Planova: A validatable membrane for the effective removal of viruses', *Proceedings of Euromembrane '95*, 18-20 September, University of Bath, Bath, UK, eds. Bowen R, Field RW and Howell JA, Centre for Continued Education Publishing, Chippenham, UK, **VOL 2**, 347-351.

**Shorrock CJ and Bird MR(1998),** 'Membrane cleaning: Removal of irreversibly fouled yeast deposits', *Trans IChemE*, Part C, **76**, 30 - 38.

**Smith KE (1990),** 'Cleaning and sanitising of spiral-wound polysulphone membranes', *Ph.D Thesis*, University of Wisconsin, Madison, USA.

**Smith KE and Bradley RL (1986),** 'Effective cleaning of polysulphone ultrafiltration membrane systems and corrosion by bisulphate used as a sanitiser', *Journal of Dairy Science*, **69**, 1232-1240.

**Stairmand JW and Bellhouse BJ (1985),** 'Mass transfer in a pulsating turbulent flow with deposition into furrowed walls', *Journal of Heat Mass Transfer*, **27**, 1405-1417.

**Strange ED, Malin EL, Van Hekken DL And Basch JJ (1992),** 'Chromatographic and electrophoretic methods used for analysis of milk-proteins', *Journal Of Chromatography*, **624**, 81-102.

**Suki AB, Fane AG and Fell CJD (1984),** 'Flux decline in protein ultrafiltration', *Journal of Membrane Science*, **21**, 269-283.

**Taddei C, Aimar P, Daufin G and Sanchez V (1988)**, 'Factors affecting fouling of an inorganic membrane during sweet whey ultrafiltration', *Le Lait*, **68**, 157-176.

**Tarleton ES and Wakeman RJ (1994)**, 'Understanding flux decline in crossflow microfiltration: Part II - Effects of process parameters', *Trans IChemE*, **72**, 431-440

**Tragardh G (1989)**, 'Membrane cleaning', *Desalination*, **71**, 325-335.

**Tragardh G (1991)**, 'Membrane Applications in the Food Industry', *Polymer Journal*, **23**, 521-529.

**Tzeng WC and Zall RR (1990)**, 'Combining polymers with chemical, thermal and turbulent conditions to clean and ultrafiltration membrane fouled with milk', *Process Biochemistry International*, **June**, 71-78.

**Vetier C, Benasar M and De La Fuente BT (1988)**, 'Study of the fouling of a mineral microfiltration membrane using scanning electron microscopy and physiochemical analyses in the processing of milk', *Journal of Dairy Research*, **55**, 381-400.

**Wagner J (1996)**, *Membrane filtration handbook: Practical tips and hints*, Wagner Publishing, Aps, Denmark.

**Wahlgren M and Arnebrant T (1989)**, 'Protein adsorption on to polysulfone surfaces and some aspects on fouling of membranes', *Fouling and Cleaning in Food Processing*, eds. Kessler HG and Lund DB, Munich, FRG, 200-205.

**Wakeman RJ and Tarleton ES (1991)**, 'An experimental study of electroacoustic crossflow microfiltration', *Trans IChemE*, **69**, 386-397.

**Wenten IG, Rasmussen A and Jonsson G (1994)**, 'Membrane cleaning after beer clarification', *Proceedings from the Fouling and Cleaning in Food Processing Conference*, Jesus College Cambridge, European Commission Publishing, Brussels, 188-195.

**Whitaker C, Ridgeway H and Olson EH (1984)**, 'Evaluation of cleaning strategies for removal of biofilms from reverse osmosis membranes', *Applied and Environmental Microbiology*, **48**, 395-404.

**Winfield BA (1986)**, 'Waste treatment by reverse osmosis membranes', *Membrane Separations in Biotechnology*, ed. McGregor WC, 355-371.

**Wright KIT, Cui ZF and Pepper D(1995)**, 'The filtration characteristics of proteins in conventional and sparged crossflow ultrafiltration', *IChemE Research Event*, University of Edinburgh, Edinburgh, UK, 1145-1147.

**Xiong YL, Dawson KA and Wan L (1993)**, 'Thermal aggregation of β-lactoglobulin: Effect of pH, ionic environment and thiol reagent', *Journal of Dairy Science*, **76**, 70-77.

**Yamagiwa K, Kobayashi H, Ohkawa, A and Onodera M (1993)**, 'Effect of anti-foam fouling on solute rejection by ultrafiltration membrane', *Journal of Chemical Engineering of Japan*, **26**, 18-20.

**Yamagiwa K, Kobayashi H, Ohkawa A Onodera M, Ohkawa A, Kamiyama Y and Tasaka K (1994)**, 'Surfactant pre-treatment of a polysulphone ultrafilter for reduction of antifoam fouling', *Biotechnology and Bioengineering*, **4**, 301-308.

**Yip V, Arnfield SD and Hydamaka AW (1996)**, 'Potential for stainless steel microfiltration processing to reduce effluent from a fluid milk and ice cream processing plant', *Journal of Dairy Science*, **79**, 710-716.

**Zhu BH and Chen P (1993)**, 'The industrial application of ultrafiltration membranes', *Desalination*, **90**, 119-126.

# APPENDIX I

# SOLUTION PROPERTY MEASUREMENT

## DENSITY MEASUREMENT

Solution densities were measured using a 25 ml pyknometer in accordance with BS 733 (1987). The bottles precise capacity was calculated at 20°C using a constant temperature water bath (± 0.5°C) and distilled water. The density of the water was assumed to be 998 $kgm^{-3}$ [Perry (1992)], and the mass of the bottle and solution was determined using a Sartorius balance, accurate to ± 1 mg. Each solution was left to equilibrate in the water bath for 1 hour. The densities for water, 0.2, 0.5 and 1.0 wt.% sodium hydroxide solutions, as well as a 3.5 wt.% WPC solution are reported in Table A1.1 for temperatures of 20, 50 and 70°C.

*Table A1.1 Test solution density measurements ($kgm^{-3}$)*

| Solution | 20°C | 50°C | 70°C |
|---|---|---|---|
| **Water** | 998 | 986 | 977 |
| **0.2 wt.% NaOH** | 996 | 988 | 979 |
| **0.5 wt.% NaOH** | 1000 | 991 | 983 |
| **1.0 wt.% NaOH** | 1003 | 995 | 986 |
| **3.5 wt.% WPC** | 1026 | 1017 | 1008 |

## VISCOSITY MEASUREMENT

The viscosities of distilled water, 0.2. 0.5 and 1.0 wt.% sodium hydroxide solutions, as well as a 3.5 wt.% WPC solution were determined in accordance with BS 188 (1977). A glass capillary U-tube viscometer (Fisons Scientific Equipment) was used for direct flow measurements. The viscometer and the solutions were submerged in a constant temperature water bath (± 0.5°C) and the time taken for a determined volume of liquid to flow through a glass capillary was measured. The kinematic viscosity was calculated from the mean of measured flow using the following formula:

$$\eta_S = \frac{\rho_W}{\rho_S}\frac{t_S}{t_W}\eta_W \qquad \textbf{(A1.1)}$$

Where the density ($\rho_W$) and kinematic viscosity ($\eta_W$) of water at 20°C are known [Perry (1992)].

The dynamic viscosity, $\mu$ ($kgm^{-1}s^{-1}$), is then calculated from

$$\mu = \eta\rho \qquad \textbf{(A1.2)}$$

The calculated kinematic ($\eta_S$) and dynamic ($\mu$) viscosities are given in Tables A1.2 and A1.3, respectively.

*Table A1.2 Test solution kinematic viscosity ($m^2s^{-1}$)*

| Solution | 20°C | 50°C | 70°C |
|---|---|---|---|
| **Water** | $1x10^{-6}$ | $5.6x10^{-7}$ | $4.5x10^{-7}$ |
| **0.2 wt.% NaOH** | $1x10^{-6}$ | $5.6x10^{-7}$ | $4.7x10^{-7}$ |
| **0.5 wt.% NaOH** | $1x10^{-6}$ | $5.6x10^{-7}$ | $4.7x10^{-7}$ |
| **1.0 wt.% NaOH** | $1x10^{-6}$ | $5.7x10^{-7}$ | $4.7x10^{-7}$ |
| **3.5 wt.% WPC** | $1.7x10^{-6}$ | $1.4x10^{-6}$ | $6.9x10^{-7}$ |

*Table A1.3 Test solution dynamic viscosity ($kgm^{-1}s^{-1}$)*

| Solution | 20°C | 50°C | 70°C |
|---|---|---|---|
| **Water** | 0.001005 | 0.000552 | 0.000442 |
| **0.2 wt.% NaOH** | 0.001006 | 0.000552 | 0.000458 |
| **0.5 wt.% NaOH** | 0.001016 | 0.000558 | 0.000461 |
| **1.0 wt.% NaOH** | 0.001029 | 000565 | 0.000461 |
| **3.5 wt.% WPC** | 0.001791 | 0.00146 | 0.000691 |

# APPENDIX II

## WHEY PROTEIN COMPOSITION

### PRODUCT DESCRIPTION

Carbelac 35, whey protein concentrate (WPC) is a free flowing, creamy white, spray dried powder containing high quality whey proteins, concentrated from sweet dairy whey by ultrafiltration.

### PHYSICAL PROPERTIES

**Appearance** - homogeneous, free flowing powder. Non-caking under normal storage conditions.

**Colour** - creamy white

Oganophelic clean and free from off-flavours

### ANALYTICAL DATA

| Property | Amount |
|---|---|
| **Protein** | 35.5 % |
| **Moisture** | 4.0 % |
| **Fat** | 4.0 % |
| **Ash** | 6.5 % |
| **Lactose** | 50% |
| **pH** | 6.2 |
| **Solubility Index** | < 0,3 ml |
| **Scorched Particles** | Disc A |
| **Nitrite** | Absent |
| **Nitrate** | < 50 ppm |

## MICROBIOLOGICAL DATA

| Property | Amount |
|---|---|
| **Total Plate Count** | < 10000/g |
| **Coliforms** | Neg. in 1 g |
| ***E. Coli*** | Neg. in 1 g |
| **Yeasts and Moulds** | < 30/g |
| **Salmonella** | Neg. in 25 g |

## PACKAGING

Carbelac 35 is packed in multi-walled paper sacks with polythene liners to a net weight of 25 kg. The product will be labelled **Whey Protein Concentrate, Product of Ireland**. Each sack will be coded with the sack number and the date of manufacture. The product will be delivered on shrink-wrapped pallets. Carbelac 35 is also available in other pack sizes depending on customer requirements.

## STORAGE

Store under cool, clean, dry conditions, not exposed to direct sunlight and strong odours. Avoid direct contact with walls and floors.

# APPENDIX III

## CALCULATION OF LINEAR VELOCITY AND REYNOLDS NUMBER

The Reynolds Number is defined as:

$$\mathrm{Re} = \frac{du\rho}{\mu} \qquad \textbf{(A3.1)}$$

where $d$ = Diameter of channel (m)

$u$ = Average linear velocity ($ms^{-1}$)

$\rho$ = Fluid density ($kgm^{-3}$)

$\mu$ = Fluid dynamic viscosity ($kgm^{-1}s^{-1}$)

When the channel cross section is not circular the equivalent diameter of a channel, $d_e$, is used. For a rectangular cross section of height $a$ and width $b$, $d_e$ is given as:

$$d_e = \frac{2ab}{a+b} \qquad \textbf{(A3.2)}$$

and the linear flow rate, $u$, is given by

$$u = \frac{\text{volumetric flowrate}}{\text{channel area}} = \frac{Q}{abn} = \left(\frac{m^3/s}{m^2}\right) \qquad \textbf{(A3.3)}$$

So, for an insert with 9 channels of height 1 mm and width 7 mm:

$$d_e = \frac{2 \times 0.001 \times 0.007}{0.001 + 0.007} = 1.75 \times 10^{-3}\,\mathrm{m}$$

Using a flow rate of 6 l/min

$$u = \frac{6/(60 \times 1000)}{0.001 \times 0.007 \times 9} = 1.5873 \text{ms}^{-1}$$

and a 0.2 wt.% NaOH solution at 50°C, where $\rho = 988$ kgm$^3$ and $\mu = 5.52 \times 10^{-4}$ kgm$^{-1}$s$^{-1}$

$$R_e \frac{1.75 \times 10^{-3} \times 1.5873 \times 988}{5.52 \times 10^{-4}} = 4972$$

# LIST OF PUBLICATIONS

Desemination of the results, carried out in preparation for this thesis, was an integral part of the project. The work has gained an international reputation through peer review as it was presented at conferences and printed in recognised journals.

## JOURNAL PUBLICATIONS

**Bartlett M, Bird MR and Howell JA, (1995)**, 'A Qualitative model for cleaning whey protein fouled microfiltration membranes', *Journal of Membrane Science*, **105**, 147-158.

**Bird MR and Bartlett M, (1995)**, 'C.I.P. optimisation for the food industry:- Relationships between detergent concentration, temperature and cleaning time', *Trans IChemE*, **Part C**, 63-70.

## CONFERENCE PROCEEDINGS

**Bird MR and Bartlett M, (1997)**, 'Modelling flux recovery during the chemical cleaning of MF membranes fouled with whey protein solutions', *ICEF 7*, Holland, April 1997, 133-36.

**Bird MR and Bartlett M, (1996)**, 'A mathematical model to describe flux recovery characteristics during the chemical cleaning of inorganic MF membranes', *IMSTEC '96*, Sydney, November 1996.

**Bartlett M, Bird MR and Field RW, (1996)**, 'A physical model to describe fouling and cleaning synergy', *IChemE Research Event*, Leeds, 2-3 April 1996,

**Bartlett M, Bird MR and Howell JA, (1995)**, 'Fouling and cleaning synergy in crossflow membrane systems', *Euromembrane '95*, Bath, 18-20 September 1995, **Vol II**, 59-62.

*Bartlett M, Bird MR and Howell JA, (1995), 'Optimisation of whey protein removal from microfiltration membranes', *IChemE Research Event*, Edinburgh, 3-5 January 1995, 1079-1081.*

**Bartlett M, Bird MR and Howell JA, (1994)**, 'Effective cleaning of microfiltration membranes fouled during whey protein processing', *4th Bath Food Engineering Conference*, Bath, 19-21 September 1994, 35-45.

**Bartlett M, Bird MR and Howell JA, (1995)**, 'Chemical cleaning of fouled membrane systems', *IChemE Research Event*, London, 2-4 January 1994, 449-452.

## OTHER PUBLICATIONS

**Bartlett M, (1994)**, 'Membrane cleaning', *Regional Courses in Membrane Processes - Module 2*, Slovak Technical University, Bratislava, 18-29 July 1994.

**Bartlett M, Bird MR and Howell JA, (1994)**, 'Flux recovery characteristics of whey protein fouled membranes cleaned with caustic based detergents', *SERC/DTI Link Scheme Iniative, London*, June 1994.

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# An experimental study for the development of a qualitative membrane cleaning model

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**Abstract**

Studies with single, multistage and formulated cleaning regimes have been evaluated for sintered stainless steel and ceramic microfiltration membranes. Results demonstrate the existence of cleaning agent concentration and temperature optima, whilst the effect of increasing crossflow velocity showed minimal increase in flux, and increasing transmembrane pressure showed a decrease in cleaning performance. A qualitative model has been developed which describes the existence of a three species deposit with each species having different removal characteristics. An initial flux increase during cleaning is explained in terms of the removal of loosely bound material which is readily solubilised by caustic solutions. Subsequent flux recovery is explained in terms of changes in deposit morphology that occur on contact with the cleaning agent. Residual fouling, present after the cleaning procedure, accounts for losses in the pristine permeability and selectivity of the membrane.

*Keywords*: Chemical cleaning; Microfiltration; Whey proteins; Flux recovery; Removal mechanism

## 1. Introduction

Membrane separation processes have major applications within the dairy industry, being widely used in the processing of milk and whey products [1]. However the operation of pressure driven membrane processes is often limited by fouling. Although, in certain circumstances, it is possible to delay the onset and reduce the amount of fouling [2–9] it is unlikely that fouling will be completely eliminated. Therefore, membrane cleaning is an essential step in maintaining the permeability and selectivity of membrane processes.

The choice of cleaning method depends on the module configuration, the chemical and physical resistance of the membrane and ancillary equipment and the nature of the fouling. Chemical cleaning is the only viable solution for most microfiltration (MF) and ultrafiltration (UF) systems.

Standard procedures for cleaning membranes fouled with milk or whey proteins involve cycles of alkaline and acid solutions circulated through the system [10]. Current membrane cleaning procedures cut into operating time, consume reagents and in many cases degrade membranes and other system components [11–14].

Despite the importance of chemical cleaning for membrane systems there is little published information on the mechanisms involved. This paper describes work which aims to increase the fundamental knowledge of membrane cleaning by elucidating the mechanisms of whey protein removal from flat-sheet MF membranes.

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The removal of whey protein deposits from stainless steel surfaces has been evaluated [15,16] and the transfer of knowledge from hard surfaces to membrane systems is the novel approach central to this investigation. An experimental procedure has been devised in which the hard surface/membrane system cleaning similarity is high and moves away to encompass wider systems.

To determine the effectiveness of each cleaning procedure a reproducible deposit must be generated. An experimental apparatus has been designed and constructed with the intention of producing fouled membrane samples from a system which is fully defined and then to clean them in situ under controlled thermo-hydraulic conditions [17].

Initial studies with sodium hydroxide, nitric acid and the formulated caustic cleaning reagent, Ultrasil 11, have been evaluated for the removal of whey protein deposits from sintered stainless steel and ceramic microfiltration membranes. Flux recovery was the main criterion used to assess membrane performance. Visual examination, by scanning electron microscopy (SEM) and X-ray micro-analysis of the deposit before, during and after cleaning has also been used to describe, the flux recovery in terms of deposit removal.

## 2. Experimental

### 2.1. Apparatus

The cleaning and fouling apparatus developed is shown in Fig. 1. The rig incorporates a stainless steel module designed to house any flat sheet membrane of $100 \times 100$ mm [18].

A 150-l cleaning solution tank, a 60-l protein solution tank and a 250-l clean water tank are connected to a multistage centrifugal pump (Lowara SV208T11M). Circulating flow-rate was measured using calibrated rotameters. A replaceable, perspex, module-insert allowed channel geometry and hence crossflow velocity to be controlled. Inlet, outlet and permeate pressures were controlled by regulating valves and measured using pressure transducers. The use of a thermostat-regulated water bath and a Gallenkamp oil bath (BLC-750) allowed accurate temperature control. The temperature was measured using platinum thermocouples and a multichannel display unit.

Permeate flux was measured using bubble flow meters [19] and/or a calibrated load cell and a stop watch.

### 2.2. Materials and methods

Initial studies have been carried out using sintered stainless steel (2 $\mu$m nominal pore size, Pall Filtration Ltd.) and ceramic (0.1 $\mu$m nominal pore size, Ceramesh Ltd.) microfiltration membranes. Distilled water (pH 5.5, $Ca^{2+} < 20$ ppm) was used to make up all process solutions throughout the study.

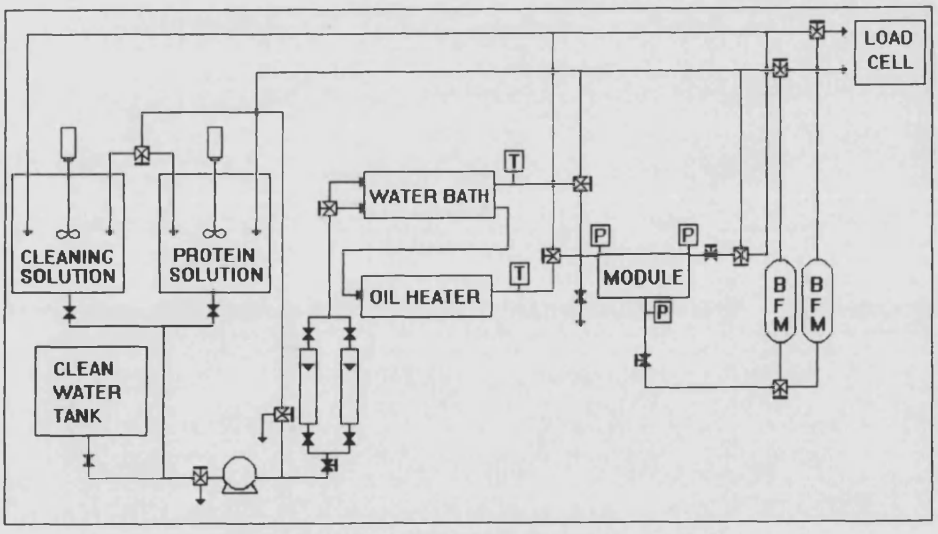


Fig. 1. Schematic diagram of fouling and cleaning rig.

*Membrane conditioning and water flux*

Used and restored membranes were conditioned by circulating a 50mM solution of sodium nitrate (Sigma Laboratories Ltd.) at 50°C with a transmembrane pressure (TMP) of 0.5 bar and a crossflow velocity (CFV) of 1.6 m $s^{-1}$ for 1 h. Immediately after conditioning, the system was adjusted to the experimental cleaning conditions and the water flux ($J_w$) was recorded. This value was used as a reference for the membrane permeability/cleanliness during each cleaning procedure.

*Membrane fouling*

After conditioning, the membrane sections were fouled using a reconstituted whey protein concentrate powder (WPC) (Carbelac 35, Carbery Milk Products) for 1 h. 20 l of a 3.5 wt% protein solution (pH 6.4) was employed for each experimental run. Both retentate and permeate were recirculated back to the feed tank. Permeate flux during the microfiltration operation ($J_f$) was monitored to check the progression of the fouling process and to ensure that a reproducible and sufficiently severe deposit was generated.

*Caustic membrane cleaning*

Systematic studies on the effects of sodium hydroxide (Sigma Laboratories Ltd.) concentration, temperature, CFV and TMP were carried out for both membrane types. Chemical cleaning was carried out for 30 min, with full recycle, followed by rinsing with distilled water for a further 30 min (no recycle). The permeation rate during cleaning ($J_c$) and rinsing was monitored and used to evaluate the % flux recovery.

*Multistage membrane cleaning*

Alkali/acid sequence cleaning has been evaluated in terms of flux recovery for the ceramic membrane:

Fouled membrane samples were cleaned by recycling 0.2 wt% sodium hydroxide solution for 30 min. A 10 min rinse with distilled water was followed by circulating 0.3 wt% nitric acid solution for a further 30 min. A final 10 min rinse with distilled water completed the procedure.

Alternatively the samples were cleaned by recycling 0.3 wt% nitric acid for 30 min followed by 10 min flushing with distilled water [10]. Further cleaning with 0.2 wt% sodium hydroxide for 30 min followed by a 10 min flush with distilled water under the same conditions completed the acid/alkali sequence.

Table 1
Formulated cleaning agent conditions

| Cleaning agent | Concentration (wt%) | pH | Temperature (°C) |
|---|---|---|---|
| NaOH | 0.4 | 13 | 50 |
| $HNO_3$ | 0.3 | 1.35 | 50 |
| Ultrasil 11 | 0.5 | 11.65 | 50 |

*Formulated membrane cleaning*

The Ultrasil 11 (Henkel Chemicals Ltd.) was evaluated, using the manufacturers recommended cleaning conditions, as shown in Table 1. Using a ceramic membrane its cleaning efficiency was compared to sodium hydroxide solution and a 0.3 wt% nitric acid solution.

*Membrane restoration*

In cases where the test cleaning procedure did not restore the water flux to its initial value the membrane was cleaned using the following standard procedure:

A 0.5 wt% solution of Ultrasil 11 was circulated at 10 l $min^{-1}$ at a temperature of 50°C with the permeate line fully closed for 20 min. The system was then flushed with distilled water using the same flow conditions and temperature for 10 min. A fresh solution of Ultrasil 11 was then circulated at 10 l $min^{-1}$ at temperature of 50°C with a TMP of 1 bar for 20 min with the permeate line open, then flushed with distilled water under the same conditions for a further 10 min.

### 2.3. Evaluation of cleaning efficiency

The cleaning efficiency was evaluated by the ratio of flux during cleaning ($J_c$) to the water flux measured under the same conditions ($J_w$) for each cleaning procedure. The percent flux recovery ($\%J_r$) was defined as

$$\%J_r = (J_c/J_w) \times 100 \quad (1)$$

### 2.4. Visualisation of the cleaning process

The use of SEM provides a more detailed visual indication of the state of the membrane surface before, during and after cleaning. Specimens prepared by air and vacuum drying were stuck to SEM stubs with conductive paste. The membrane samples were then sputter coated with a thin layer of gold or carbon before view-

ing. The specimens were viewed with a JSM 6310 scanning electron microscope in combination with a microanalysis system, LINK AN10000 (Oxford Instruments). Initial analyses have been purely qualitative; a quantitative determination of elements will form the basis of a further study.

## 3. Results

### 3.1. Fouling behaviour of membranes

Typical flux declines during the microfiltration of reconstituted whey protein solution are shown in Fig. 2a for the sintered stainless steel membrane and Fig. 2b for the ceramic membrane. As might be expected

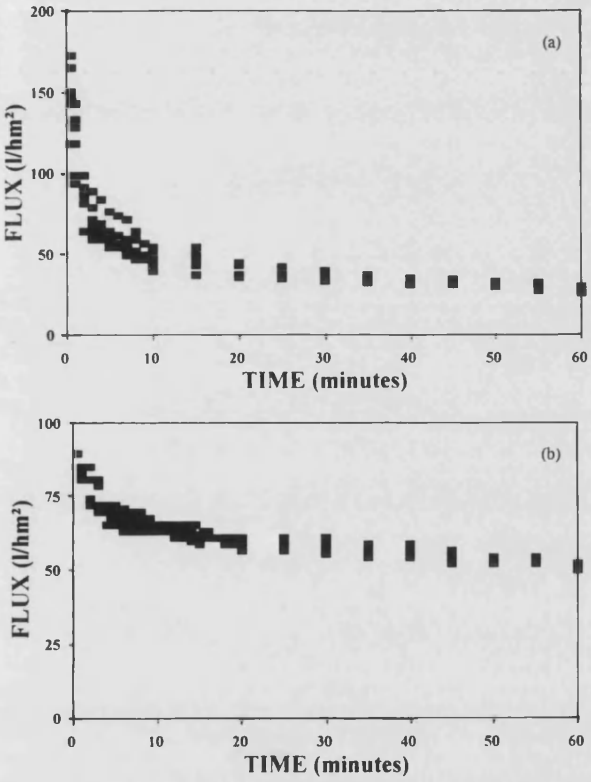


Fig. 2. (a) Microfiltration of a 3.5 wt% protein solution using a 2 μm sintered stainless steel membrane at 50°C, TMP 1 bar, CFV 1.0 m $s^{-1}$ for 1 h (×5). Water flux ~1800 l/h $m^2$ bar. (b) Microfiltration of a 3.5 wt% solution protein using a 0.1 μm ceramic membrane at 50°C, TMP 1 bar, CFV 1.0 m $s^{-1}$ for 1 h (×5). Water flux ~470 l/h $m^2$ bar.

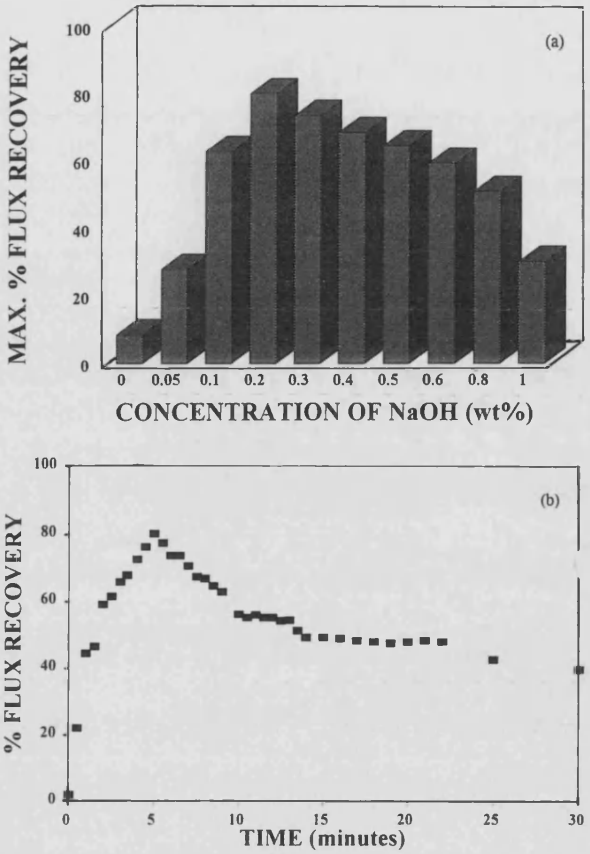


Fig. 3. (a) Effect of sodium hydroxide concentration on maximum flux recovery using a 2 μm sintered stainless steel membrane at 50°C, TMP 0.5 bar, CFV 1.6 m $s^{-1}$. (b) Typical flux recovery curve for WPC removal from a 2 μm sintered stainless steel membrane at 50°C, TMP 0.5 bar, CFV 1.6 m $s^{-1}$ using a 0.2 wt% NaOH solution.

the permeation rate for the WPC solution was much lower than the measured water flux. For both membrane types flux decline occurred quickly and the fouling was rapid, after the 1 hour fouling period the flux was less than 12% of the initial water flux. SEM shows a cake deposit of aggregates embedded in, and covered by, a "sheet-like" matrix (Fig. 10a)

### 3.2. Efficiency of sodium hydroxide cleaning

Figs. 3a and b shows the effect of sodium hydroxide concentration upon the maximum flux recovery at 50°C with a crossflow velocity of 1.6 m $s^{-1}$ and TMP of 0.5 bar for the sintered stainless steel membrane.

Using distilled water to clean the membranes results in only a small flux recovery. This indicates that the WPC deposits have low water solubility and that the

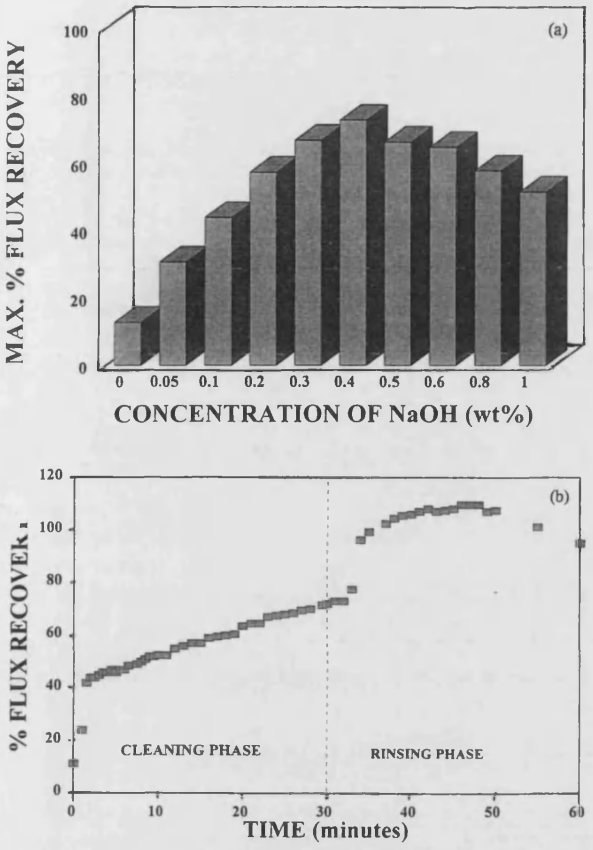


Fig. 4. (a) Effect of sodium hydroxide concentration on flux recovery using a 0.1 $\mu$m ceramic membrane at 50°C, TMP 0.5 bar, CFV 1.6 m s$^{-1}$. (b) Typical flux recovery curve for WPC removal from a 0.1 $\mu$m ceramic membrane with TMP 0.5 bar, CFV 1.6 m s$^{-1}$ at 50°C using a 0.4 wt% NaOH solution.

material is so tightly bound that removal by fluid mechanical shear alone is not possible. As the sodium hydroxide concentration is increased, so the maximum flux recovery increases dramatically. For the sintered stainless steel membrane the use of 0.2 wt% sodium hydroxide results in a maximum flux recovery of 80% of the initial water flux. A typical flux recovery curve obtained during cleaning (Fig. 3b) shows that an initially low flux value is quickly increased to a maximum value before decaying back towards a terminal flux value. This phenomena has also been reported for the removal of whey deposits from cellulose acetate UF membranes [20].

For the ceramic membrane an optimum concentration of 0.4 wt% resulted in a maximum flux recovery of 73%, after 30 min cleaning (Fig. 4a). During the cleaning phase (Fig. 4b) a sharp flux increase occurred within the first 3 min. The flux increased only gradually during the following 20 min of the cleaning cycle. Flux again increased during the early stages of the rinsing phase with a gradual decline as the rinsing progressed, possibly due to the effects of pH [21–23], and/or the compaction of the residual fouling with time [7,24].

For both membrane systems, increases in sodium hydroxide concentration above the optimum value do not aid the cleaning process but result in lower maximum flux recovery values. Kim et al. [25] noted that for concentrations of sodium hydroxide above 0.4 wt% there was reduced cleaning efficiency for milk deposit removal from UF membranes. However, Tzeng and Zall [26] reported an optimum sodium hydroxide concentration of 0.8 wt% for whole milk removal and 1.0

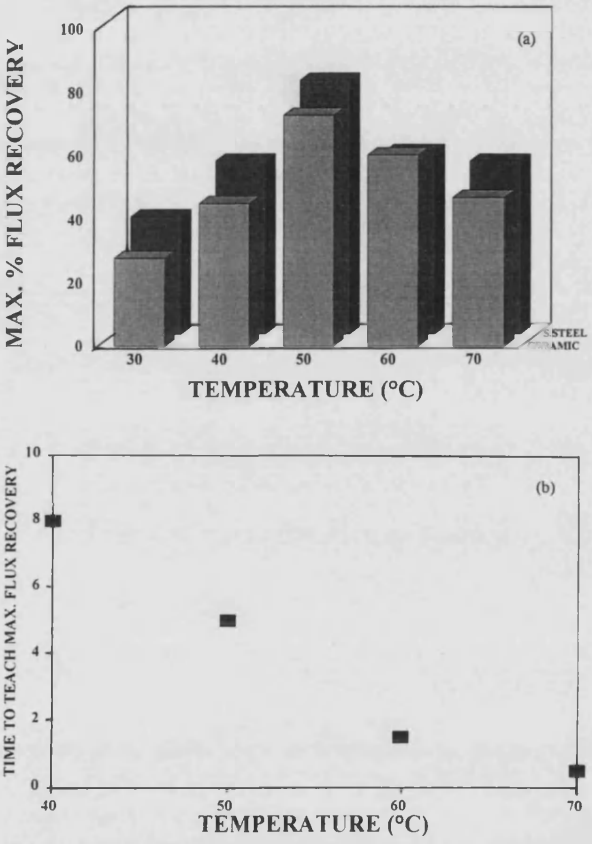


Fig. 5. (a) Effect of temperature on maximum flux recovery using a 0.2 wt% sodium hydroxide solution with the sintered stainless steel membrane and a 0.4 wt% solution for the ceramic membrane. TMP of 0.5 bar, CFV of 1.6 m s$^{-1}$. (b) Effect of temperature on time to reach maximum flux recovery for a 2 $\mu$m sintered stainless steel membrane cleaned with a 0.2 wt% sodium hydroxide solution using a TMP of 0.5 bar and a CFV of 1.6 m s$^{-1}$.

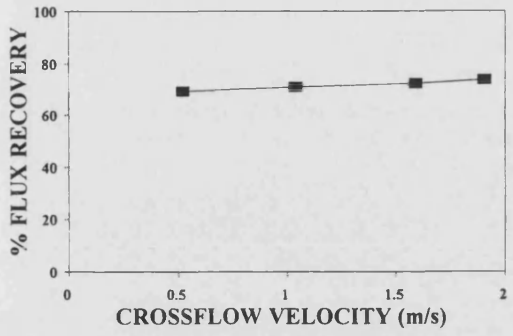


Fig. 6. Effect of CFV on flux recovery using a 0.4 wt% sodium hydroxide solution at 50°C with a TMP of 0.5 bar for a 0.1 μm ceramic membrane.

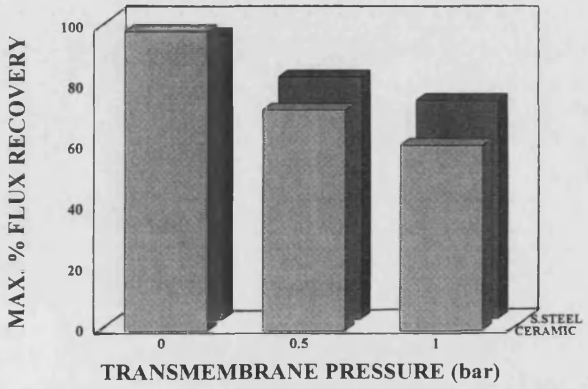


Fig. 7. Effect of TMP on flux recovery for a 2 μm sintered stainless steel membrane cleaned with 0.2 wt% sodium hydroxide and a 0.1 μm ceramic membrane cleaned with 0.4 wt% sodium hydroxide. Both membranes were cleaned at a temperature of 50°C and a CFV of 1.6 m $s^{-1}$.

wt% for skim milk removal based on regression analysis of their experimental results.

The effect of temperature in the range of 30–70°C was investigated at the optimum sodium hydroxide concentrations of 0.2 wt% for the sintered stainless steel membrane and 0.4 wt% for the ceramic membrane. An optimum temperature of 50°C was found for both systems, as shown in Fig. 5a. Further increases in temperature resulted in lower maximum flux values. The time taken to reach the maximum decreased with increasing temperature. For the sintered stainless steel membrane the time taken to reach the maximum flux recovery fell from 8 min at 40°C to 30 s at 70°C (Fig. 5b).

Crossflow velocities (Fig. 6) have been examined to investigate the effect of changing the cleaning solution flow from laminar to turbulent conditions. The optimum concentration of 0.4 wt% sodium hydroxide and a temperature of 50°C were employed using a ceramic membrane for all experiments. The results show little improvement in flux recovery with increasing CFV, confirming the work of several researchers who have reported that variation in crossflow velocity

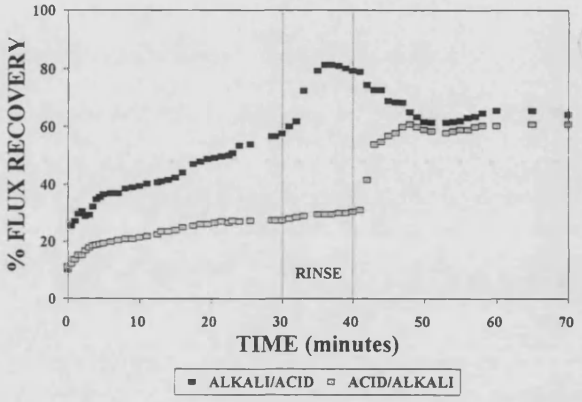


Fig. 8. Effect of alkali/acid sequence upon a 1 μm ceramic membrane cleaned using 0.3 wt% nitric acid and 0.2 wt% sodium hydroxide at 50°C with a TMP of 0.5 bar and a CFV of 1.6 m $s^{-1}$.

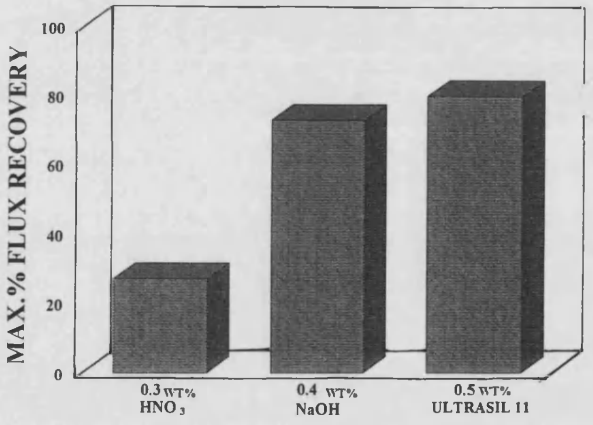


Fig. 9. Efficiency of simple and formulated cleaning chemicals for the removal of WPC deposits from a 0.1 μm ceramic membrane at 50°C with a TMP of 0.5 bar and a CFV of 1.6 m $s^{-1}$.

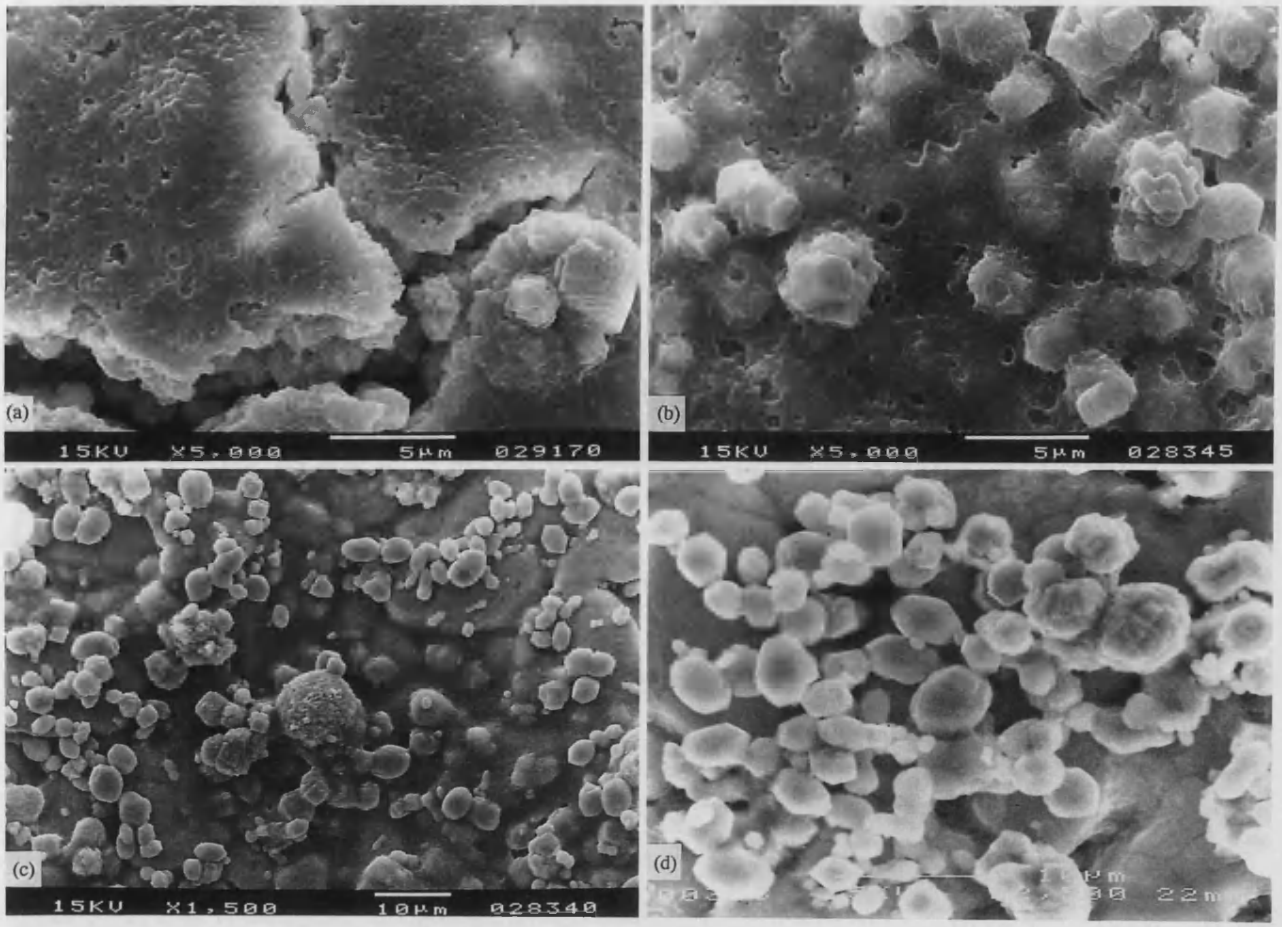


Fig. 10. (a–d) Initial stages of deposit removal from a sintered stainless steel membrane by caustic cleaning. (d–f) Continued caustic cleaning removes surface deposit. (g) Removal of the remaining mineral deposit in the final stages of cleaning. (i) Effect of 1.0 wt% sodium hydroxide on deposit morphology.

had a negligible effect upon the flux recovery achieved [25,27,28].

Zero TMP produces the highest flux recovery values after a 30 min cleaning period for both the sintered stainless steel and the ceramic membranes (Fig. 7). The flux recovery after cleaning for both systems, was sustained during the rinsing phase. The application of a TMP greater than zero resulted in lower flux recoveries.

### 3.3. Efficiency of acid/alkali sequence cleaning

The effects of alkali/acid sequence cleaning are shown in Fig. 8. Initial cleaning with 0.3 wt% nitric acid resulted in a low but sustainable flux recovery with little further flux recovery during the rinsing phase. A following alkali clean with 0.2 wt% sodium hydroxide resulted in a flux recovery of 60%.

Alternatively, cleaning with 0.2 wt% sodium hydroxide first resulted in a flux recovery of 58%. A further operation with 0.3 wt% nitric acid gave a final flux recovery of 64%.

### 3.4. Efficiency of formulated cleaning agents

Fig. 9 demonstrates the efficiency of a formulated cleaning agent for WPC removal from the ceramic membrane compared to simple cleaning chemicals. Cleaning procedures with Ultrasil 11, a caustic based membrane cleaning reagent with the addition of surfactants, gave the highest flux recovery of 80%.

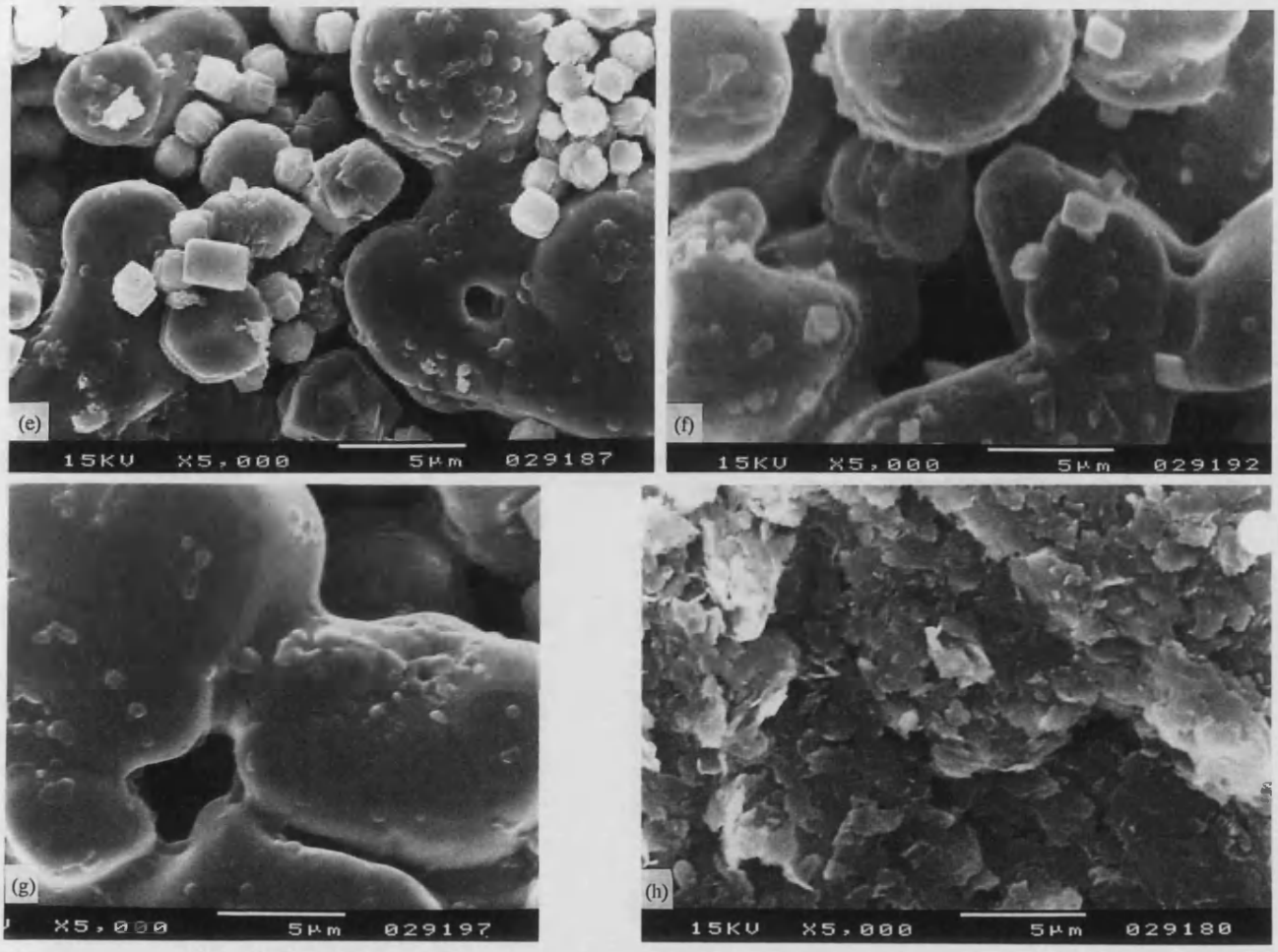


Fig. 10 (continued).

### 3.5. *Visualisation of the cleaning process*

SEM of the fouled membrane samples has shown the surface deposit to be a ''sheet-like'' deposit (Fig. 10a) which is removed within the first few minutes of cleaning with sodium hydroxide (Fig. 10b). Its removal reveals a deposit of aggregates and minerals embedded in a matrix (Fig. 10c). X-ray micro-analysis reveals that the deposit at this point has a high calcium content.

With continued caustic cleaning the matrix and aggregates are removed, as shown in Figs. 10d and e, such that the surface of the membrane appears relatively free of deposit (Fig. 10f). At this stage, after caustic cleaning, only mineral deposit can be seen on the surface of the membrane.

Examination of membranes cleaned with Ultrasil 11 show that the mineral deposit is removed (Fig. 10g). X-ray micro-analysis of the membrane samples after cleaning procedures with either caustic or Ultrasil 1' revealed a small amount of organic matter which was not visible on the surface.

Examination of the deposit on contact with a 1.0 wt% sodium hydroxide solution revealed changes in the surface morphology which may explain the reduced flux recovery values found experimentally with concentrations above the optima (Fig. 10h).

## 4. Discussion

The characteristic curve shape for flux recovery resulting in a sharp increase in flux during the first few

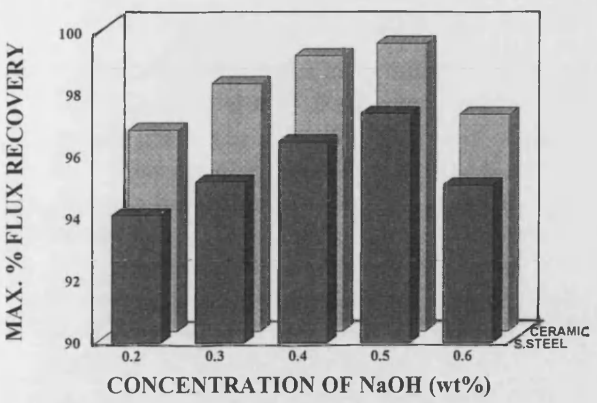


Fig. 11. Effect of sodium hydroxide concentration on flux recovery with zero TMP, a temperature of 50°C and a CFV of 1.6 m $s^{-1}$ for 0.1 μm ceramic membrane and a 2 μm sintered stainless steel membrane.

minutes can be explained by the removal of deposit easily solubilised by sodium hydroxide. Several researchers [29–32] have described this sheet-like deposit as being composed primarily of the whey protein β-lactoglobulin. This observation is further corroborated by the poor flux recovery values obtained after cleaning with nitric acid where the presence of protein on the surface reduces the acids ability to penetrate the cake and remove any mineral components in the deposit.

The apparent differences in flux recovery for the two membrane types may be explained by changes in deposit morphology on contact with the sodium hydroxide and pore size effects when the deposit is subjected to pressure. Concentration optima found when cleaning food based deposits from hard surfaces have been described in terms of changes the deposit undergoes on contact with sodium hydroxide [16,33]. The deposit becomes swollen; the swelling increasing to a point where the maximum voidage occurs at the optimum concentration. Further increases in concentration lead to a reduction in the deposit voidage. On the membrane surface, as the deposit swells and the voidage increases, the deposit may become less rigid.

When cleaning the stainless steel membrane the use of an applied TMP may force the fragile deposit into the pore structure of the membrane where it may be compacted over time to give a declining flux value. Using a concentration above 0.2 wt% for cleaning results in a faster approach to the highest voidage and a faster decline from the maximum flux recovery.

With decreasing pore size the cake is less susceptible to the effects of TMP and relatively more susceptible to surface erosion, thus, a higher optimum concentration is observed (0.4 wt%).

As a result of these observations further experiments were carried out to investigate the effect of sodium hydroxide concentration on the removal of WPC deposit employing zero TMP (Fig. 11). The results show an optimum sodium hydroxide concentration for proteinaceous deposit removal of 0.5 wt%. This optimum concentration value is the same as that found for hard surface protein removal [16]. This may be due to the absence of an applied pressure to force the increasingly compressible deposit into the pores.

An optimum temperature of 50°C, observed for the cleaning of fouled membranes, may, also, be explained in terms of the structure of the swollen deposit. At low temperatures any increase will speed up the chemistry of the deposit breakdown and dissolution, while decreasing the cleaning solution viscosity and hence increasing the Reynolds number. At extremes of pH and temperature new protein/protein interactions lead to precipitation, solidification or gel formation which are not susceptible to break down [34]. At temperatures above 50°C calcium shows decreasing solubility [10]. This may prevent its removal from the membrane or cause redeposition of insoluble calcium salts on the membrane surface.

It is commonly suggested that a TMP less than that used for the microfiltration operation should be used during the cleaning procedure. These results demonstrate that any applied pressure during cleaning will not result in maximum cleaning efficiency while there is surface deposit present.

No optimal relationship was found for CFV within the scope of this study. These results agree with findings of other workers [25,27] who reported that cleaning performance was not a strong function of the surface shear rate or the CFV. This indicates that changes in CFV primarily affect the removal of dissolved material. Thus the decline in flux during the cleaning procedure may be further accentuated by the presence of partially hydrolysed protein at the surface and in the pores of the membrane when cleaning using relatively low crossflow velocities

## 5. Implications for modelling

As a result of the systematic experimental study and the mechanisms discussed to describe the observed results, a qualitative model for the removal of a 3 species deposit has been hypothesised which facilitates a partial separation of the fluid mechanics and chemistry of the cleaning process.

Species 1 is loosely bound proteinaceous material which is easily solubilised by low concentration sodium hydroxide solutions. Species 2 which is more tightly bound, and may also be present in the pores of the membrane. Species 2 may swell on contact with sodium hydroxide resulting in a deposit, with different permeation characteristics, depending on the concentration and temperature of the sodium hydroxide. This deposit may be more or less susceptible to fluid mechanic effects depending on the morphological changes that have occurred. If a large pore microfiltration membrane is used Species 2 may be compacted within the membrane pores resulting in further flux losses. The modified deposit may be more easily solubilised by water, as is shown by the sharp increase in flux during the rinsing stage of cleaning. Species 3 is more resistant to the cleaning and rinsing process. The residual fouling accounts for the loss in the pristine permeability and selectivity characteristics of the membrane.

## 6. Conclusions

Optimising the fluid mechanics and chemistry of cleaning should lead to a reduction in cleaning time and less destructive cleaning processes. A systematic experimental study has shown that concentration and temperature optima exist for the removal of proteinateous deposit from fouled membranes by sodium hydroxide.

Utilising an applied pressure force during cleaning results in an observed optimum sodium hydroxide concentration of 0.2 wt% for deposit removal from the sintered stainless steel membrane. With decreasing pore size the deposit is less likely to be forced into the pores of the membrane during cleaning where it would be susceptible to the compaction by an applied TMP force and relatively more susceptible to surface erosion effects. Thus, for the ceramic membrane a higher optimum concentration was observed (0.4 wt%). Further experiments employing a TMP of zero have shown a concentration optimum of 0.5 wt% sodium hydroxide, for both membrane types. This is the same value as found for hard surface protein removal [16]. Thus, zero transmembrane pressure is recommended for maximum efficiency in deposit removal during the initial stages of the cleaning procedure.

An optimum temperature of 50°C was found for both membrane types. While turbulent conditions promote mixing and surface erosion it may prove more economic to use less demanding flow conditions.

It is clear from experiments with alkali/acid regimes, and the formulated membrane cleaner, that to achieve the optimum cleaning efficiency and reduce cleaning time an alkali based cleaning agent should be used for the removal of a primarily proteinateous deposit. The results suggest the use of a caustic based multicomponent cleaning agent would provide efficient cleaning of inorganic microfiltration membranes in an optimised cleaning regime.

A qualitative model has been developed to explain the experimental flux recovery values and the existence of cleaning agent concentration and temperature optima.

## Acknowledgements

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## References

[1] J.L. Maubois, Novel valorisation of dairy components, Agro Ind. Hi-Technol., 1 (1990) 25.
[2] J.A. Howell and S.M. Finnigan, Hydrodynamics and Membrane Filtration, Effective Industrial Membrane Processes – Benefits and Opportunities, 1991, pp. 49–60.
[3] W.R. Bowen and H.A.M. Sabuni, Pulsed Electrophoritic Membrane Cleaning, Ind. Chem. Eng. Res. Event, (1992) 92–94.
[4] V. Chen, A.G. Fane and C.J.D. Fell, The use of anionic surfactants for reducing fouling of ultrafiltration membranes: their effects and optimisation, J. Membrane Sci., 67 (1992) 249–261.
[5] L.E.S. Brink, S.J.G. Elbers, T. Robbertsen and P. Both, The anti-fouling action of polymers preadsorbed on ultrafiltration and microfiltration membranes, J. Membrane Sci., 76 (1993) 281–291.

[6] A.R. Da Costa, A.G. Fane and D.E. Wiley, Ultrafiltration of whey protein solutions in spacer-filled flat channels, J. Membrane Sci., 76 (1993) 245–254.
[7] M.R. Mackley and N.E. Sherman, Cake filtration mechanisms in steady and unsteady flows, J. Membrane Sci., 77 (1993) 113–121.
[8] C.W. Robinson, M.H. Siegel, A. Condemine, C. Fee, T.Z. Faridy and B.R. Glick, Pulsed-electric-field crossflow ultrafiltration of bovine serum albumin, J. Membrane Sci., 80 (1993) 209–220.
[9] Q. Gan and J.A. Howell, Fouling and backflush in beer clarification using ceramic membranes food process engineering, 4th Bath Food Engineering Conference, University of Bath, 19–21 September 1994,
[10] G. Tragardh, Membrane Cleaning, Desal., 71 (1989) 325–335.
[11] R. Chong, P. Jelen and W. Wong, The effect of cleaning agents on a noncellulosic ultrafiltration membrane, Sep. Sci. Technol., 20 (1985) 393–402.
[12] D.R. Kane and N.E. Middlemass, Cleaning chemicals – state of the knowledge, in D. Lund, E. Plett and C. Sandu (Eds.), Fouling and Cleaning in Food Processing, 1985, pp. 312–335.
[13] K.E. Smith and R.L. Bradley, Ineffective cleaning of polysulfone ultrafiltration membrane systems and corrosion by bisulfate used as a sanitiser, J. Dairy Sci., 69 (1986) 1232–1240.
[14] H.F. Bohner and R.L. Bradley, Effective cleaning of polysulfone ultrafiltration systems, J. Dairy Sci., 75 (1992) 718–724.
[15] M.R. Bird and P.J. Fryer, An experimental study of the cleaning of surfaces fouled by whey proteins, Trans. IChemE, Part C, 69 (1991) 13–21.
[16] M.R. Bird, Cleaning of Food Process Plant, Ph.D. Thesis, University of Cambridge, 1993.
[17] M. Bartlett, M.R. Bird and J.A. Howell, Chemical cleaning of fouled membrane systems, Ind. Chem. Eng. Res. Event, (1994) 449–452.
[18] P. Aimar, J.A. Howell and M. Turner, Effects of concentration boundary layer development on the flux limitations of ultrafiltration, Chem. Eng. Des. Res., 67 (1989) 255–261.
[19] J.T. Bishop and N. Sanders, Bubble flow meter for measurement of low permeate flows in ultrafiltration, Biotechnol. Technol., 3 (1989) 101–106.
[20] M.F. Parkin and K.R. Marshall, The cleaning of tubular cellulose acetate ultrafiltration membranes, N. Zealand J. Dairy Sci. Technol., 11 (1976) 107–113.
[21] M.S. Le, Membrane Ultrafiltration: Fouling and Treatment Ph.D. Thesis, University of Swansea, 1982.
[22] P.R. Heinemann, The Problem of Fouling in Crossflow Microfiltration Ph.D. Thesis, University of Bath, 1987.
[23] R.J. Lahiere and K.P. Goodboy, Ceramic membrane treatment of petrochemical waste water, Environ. Prog., 12 (1993) 86–96.
[24] J. Lindau and A.S. Jonnson, Cleaning of ultrafiltration membranes after treatment of oily waste water, J. Membrane Sci., 87 (1994) 71–78.
[25] J.-K. Kim, P. Sun, V. Chen, D.E. Wiley and A.G. Fane, The cleaning of ultrafiltration membranes fouled by whey protein, J. Membrane Sci., 80 (1993) 241–249.
[26] W.C. Tzeng and R.R. Zall, Combining polymers with chemical, thermal, turbulent conditions to clean an ultrafiltration membrane fouled with milk, Proc. Biochem. Int., (1990) 71–78.
[27] G. Daufin, U. Merin, J.P. Labbé, A. Quémerais and F.L. Kerhervé, Cleaning of inorganic membranes after whey and milk ultrafiltration, Biotechnol. Bioeng., 38 (1991) 82–89.
[28] G. Daufin, U. Merin, F.L. Kerhervé, J.P. Labbé, A. Quémerais and C. Bousser, Efficiency of cleaning agents for an inorganic membrane after milk ultrafiltration, J. Membrane Sci., 59 (1992) 29–38.
[29] D.N. Lee and R.L. Merson, Examination of cottage cheese whey proteins by scanning electron microscopy: relationship to membrane fouling during ultrafiltration, J. Dairy Sci., 58 (1975) 1423–1432.
[30] T.J. Nisbet, T.M. Thorn and P.W. Wood, Observations on the fouling of polysulfone ultrafiltration membranes by acid whey, N. Zealand J. Dairy Sci. Technol., 16 (1981) 113–120.
[31] C. Vetier, M. Bennasar and B.T. De la Fuente, Study of fouling of a mineral micro-filtration membrane using scanning electron microscopy and physiochemical analysis in the processing of milk, J. Dairy Res., 55 (1988) 381–400.
[32] G. Gésan, G. Daufin, U. Merin, J.P. Labbé and A. Quémerais, Fouling during constant flux crossflow microfiltration of pre-treated whey. Influence of transmembrane pressure gradient, J. Membrane Sci., 80 (1993) 131–145.
[33] M.R. Bird, Cleaning Agent Concentration and Temperature Optima in the Removal of Food Based Deposition Fouling And Cleaning in Food Processing, Jesus College, Cambridge, 1994, pp. 21–25.
[34] T.P. Coultate, Food: The Chemistry of its Components, 2nd ed., R. Soc. Chem., 1992, pp. 85–125.

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# CIP OPTIMISATION FOR THE FOOD INDUSTRY: Relationships Between Detergent Concentration, Temperature and Cleaning Time

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Optimum cleaning agent concentrations are reported for the removal of protein, starch and glucose deposits from stainless steel surfaces, and protein deposits from microfiltration membranes using a range of cleaning agents. Optimum detergent temperatures were found in both hard surface and membrane cleaning applications. Experimental cleaning protocols and measurement techniques are discussed. Phenomena are described which are applicable in a general sense, and not present merely as an artefact of a particular system or geometry. Mechanisms to describe optimal removal phenomena are discussed. A qualitative model has been developed to explain the shape of the flux recovery curves during membrane cleaning, and the existence of both concentration and temperature optima. A knowledge of temperature and concentration optima is a necessary prerequisite to the optimisation of any CIP programme.

*Keywords: Cleaning; fouling; CIP; microfiltration; whey; carbohydrate.*

## INTRODUCTION

Cleaning of food process plant is necessary to ensure hygienic operation, in addition to maintaining a high heat transfer rate and a low system pressure drop. In membrane processes, cleaning is essential to maintain acceptable process flux values in addition to hygienic considerations. Cleaning procedures are of environmental concern due to their generation of large quantities of effluent containing potentially harmful chemical cocktails which are usually highly alkaline[1,2]. The costs associated with cleaning can be significant, and include those for cleaning chemicals, effluent disposal, pumping liquids and raising steam, in addition to the costs of lost production due to cleaning related downtime[3,4]. Elucidation of cleaning mechanisms and subsequent design of efficient cleaning protocols is therefore important for both cost and environmental impact minimisation reasons.

Three separate studies that show optimum values of cleaning agent concentration and temperature are reported. Results are presented for:

(i) the removal of whey protein deposits from stainless steel surfaces using caustic based cleaning agents,
(ii) the removal of carbohydrate (starch and glucose) deposits from stainless steel discs using a range of caustic, acidic and formulated detergent compounds, and
(iii) the cleaning of sintered steel microfiltration membranes fouled with whey proteins using sodium hydroxide.

This paper aims to illustrate the common occurrence of optimum removal behaviour by describing widespread phenomena which are not merely artefacts of a particular system of geometry.

## CLEANING OF WHEY AND WHOLE MILK DEPOSITS

In this study a novel approach was used which facilitated the qualitative and quantitative investigation of whey and whole milk protein deposit removal from stainless steel surfaces using both simple and formulated detergent systems.

Two pieces of equipment were used for fouling and cleaning experimentation. Firstly, a fouling apparatus[5] through which 0.8 litre/min of a protein solution (whole milk or 3.5 wt% whey protein) was passed at inlet temperatures of 74°C and 83°C for whey and whole milks respectively. The hot protein solution then passed through a concentric tube heat exchanger through which hot oil flowed counter-currently at an inlet temperature of 97°C in the case of whey, and 114°C for whole milk studies. These temperatures were selected such that the resulting ramp in temperature caused protein deposition along a stainless steel test section (length 2 m, internal diameter 6.05 mm) to give a reproducible and uniform deposit for use in cleaning experimentation. The whey protein deposit formed averaged 90 wt% protein, and had an average deposition mass of 97 g m$^{-2}$, and thickness of 0.15 mm. Whole milk deposit averaged a mass of 250 g m$^{-2}$, was 0.38 mm thick, and was comprised of 50 wt% protein.

Secondly, a cleaning apparatus was constructed to determine removal kinetics (Figure 1). The apparatus enabled a fouled sample to be cleaning using alkali

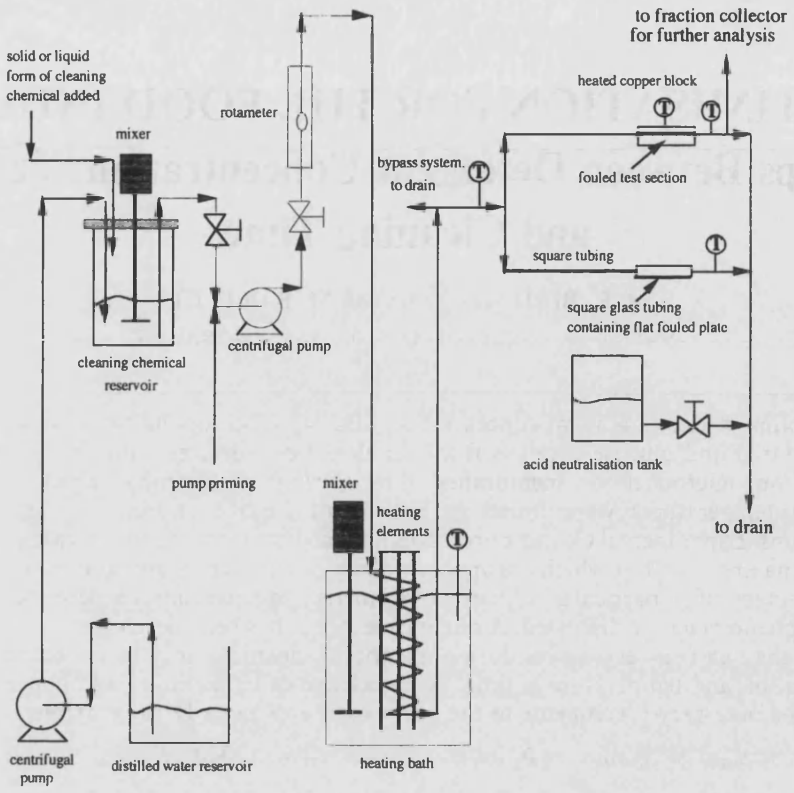


*Figure 1.* Schematic representation of the whey protein deposit cleaning apparatus.

detergents under controlled thermo-hydraulic conditions. A fouling run produced a 2 m long section, from which a dozen 15 cm long sections were produced for cleaning experimentation. Precise cleaning agent temperature control was possible in the range 30–75°C, and Reynolds numbers of 100–7600 were achieved. Samples of effluent containing the removed soil fraction were collected at regular time intervals, and deposit removal rates calculated from protein concentrations determined by a commercial Bradford dye assay[6], adapted for use with alkaline solutions. In addition, visual inspection of tube surfaces after cleaning was used to confirm that surfaces were in fact clean. On-line visualisation of the cleaning process was also possible, using a flat fouled stainless plate inserted in a rectangular glass section tube. Further details of fouling and cleaning apparatus and experimental protocols can be found in Bird and Fryer[7,8] and Bird[9].

### Whey Protein and Whole Milk Cleaning Results

A large matrix of cleaning kinetic data has been generated for milk protein deposit removal[9]. Here, a small selection of the data relating to concentration optima is discussed.

The effect that varying sodium hydroxide concentration has upon whey protein deposit removal is shown in Figure 2. In the absence of a cleaning agent, no removal is seen. Low concentrations result in long cleaning times. As the caustic concentration is increased, so cleaning times decrease until a minimum cleaning time of 10 minutes is reached at a concentration of 0.5 wt%. The range of concentrations 0.2–0.6 wt% provides the most effective cleaning. Rather than aiding the cleaning process, increases in concentration beyond 0.5 wt% result in longer cleaning times. The use of 2.0 wt% sodium hydroxide leads to a cleaning time of 50 minutes; the same duration as when 0.1 wt% sodium hydroxide is used. The existence of an optimum cleaning solution concentration was also found for cleaning whole milk soils with sodium hydroxide (Figure 3). Sodium hydroxide in the range 0.3–0.5 wt% was found to be the most effective, and once again a concentration of 0.5 wt% sodium hydroxide was found to be optimal for proteinaceous deposit removal.

Scanning electron microscopy showed that the protein deposit structure changed dramatically on contact with the cleaning solution; the high density platelet deposit structure changing to an open, hollow matrix

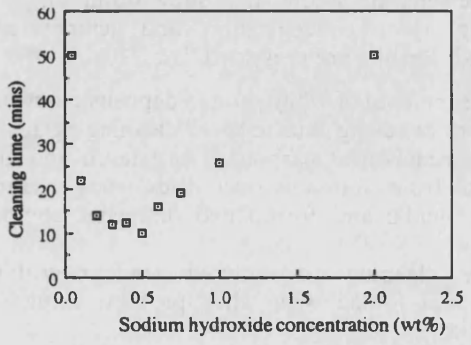


*Figure 2.* Effect of concentration upon cleaning time of a whey protein deposit cleaned using sodium hydroxide at 50°C and 0.175 m s$^{-1}$.

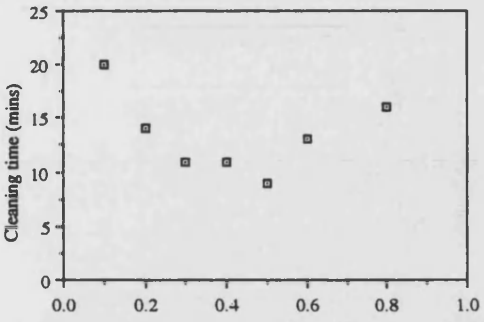


*Figure 3.* Effect of concentration upon the cleaning time of a whole milk deposit cleaned using sodium hydroxide at 50°C and 0.175 m $s^{-1}$.

after cleaning solution contact[9,10]. At the optimum concentration, the swollen deposit has the highest voidage, and is thus most susceptible to removal by fluid mechanical shear. Higher or lower cleaning agent concentrations resulted in a swollen deposit with a lower voidage, which is harder to remove. Visualisation of the cleaning process has shown that it is inherently non-uniform, and that removal occurs by the swelling and subsequent break up of the fouled layer into discrete aggregates.

## REMOVAL OF CARBOHYDRATE BASED DEPOSITION

Processing of carbohydrates into consumer products often produces viscous pastes which can lead to fouling, particularly of heat exchange surfaces. In this study both starch and glucose based deposit removal is investigated.

Whilst protein deposit removal mechanisms have been extensively studied, carbohydrate deposit removal has received little attention. Heterogeneous mixtures containing carbohydrates have been studied[11,12], but few studies on pure carbohydrate cleaning are reported.

In this paper a pilot study is presented to determine the effectiveness of a range of cleaning agents on carbohydrate removal, and to characterise cleaning agent concentration and temperature effects, rather than determine deposit removal kinetics.

### Carbohydrate Deposit Fouling Experiments

Fouling protocols have been developed which enable reproducible carbohydrate fouling deposits to be produced for use in cleaning investigations. Details of these protocols may be found in Bird *et al.*[13] Starch deposit fouling was produced by coating stainless steel discs, 2″ (5.08 cm) in diameter, 1 mm thick, with a reconstituted starch paste comprising of 84 wt% starch (dry mass). Coated discs were placed on a hot plate at a temperature of 330°C for 4 minutes, producing a deposition mass of 490 g $m^{-2}$. The deposit produced was tenacious, representing a tough cleaning problem.

A glucose fouling protocol was developed which involved the solidification of glucose from a molten solution onto stainless steel test sections of dimensions 50 × 50 × 1 mm. The glucose solution depth was controlled to produce a dry deposition mass 1200 g $m^{-2}$. Four modes of deposit cooling were investigated[13], of these quenching the molten deposit by rapid water cooling of the underside of the vessel containing the test piece was found to produce the hardest deposit, and the most difficult cleaning problem.

### Carbohydrate Deposit Cleaning Experiments, Results and Discussion

Static cleaning experiments consisting of starch deposits immersed in baths of cleaning agent showed that relying solely on cleaning agent diffusion into the deposit matrix results in an extremely slow clean. Trends in cleaning agent concentration and temperature upon removal time were required, rather than an accurate simulation of industrial practice. For this reason a 5.25 litre 40 kHz ultrasonic bath (Decon Ltd) was used to provide a reproducible mechanical effect.

*Starch deposit cleaning experiments*

A range of cleaning agents were tested on the starch samples[13], of which the most effective were found to be sodium hydroxide and nitric acid, and detailed concentration sweeps were undertaken using these compounds. Sample plates were removed after fifteen minutes cleaning time, thereby providing a snapshot of the cleaning process at this point rather than following a cleaning kinetic. Samples removed from the cleaning solution were carefully rinsed with distilled water to stop further reaction and dried in an oven to a constant mass. Gravimetric analysis using a micro-balance facilitated an accurate determination of the percentage of the deposit removed.

A sodium hydroxide concentration sweep was carried out at 60°C for 15 minutes (Figure 4). Sodium hydroxide concentrations of 9–20 wt% were investigated, and an optimum concentration was found to exist at 14 wt%. Not surprisingly, this value is very different to the optimum concentration found for cleaning protein deposits, of 0.5 wt%. A temperature sweep was carried out at 14 wt% sodium hydroxide using temperatures from 30–70°C (Figure 5). The existence of an optimum temperature of 50°C is seen.

A nitric acid sweep was carried out using concentrations from 5–20 wt% (Figure 6). In common with sodium hydroxide cleaning, an optimum concentration

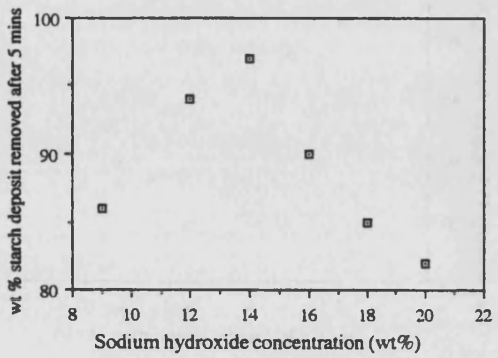


*Figure 4.* Effect of concentration upon the removal of potato starch deposit using sodium hydroxide at 60°C.

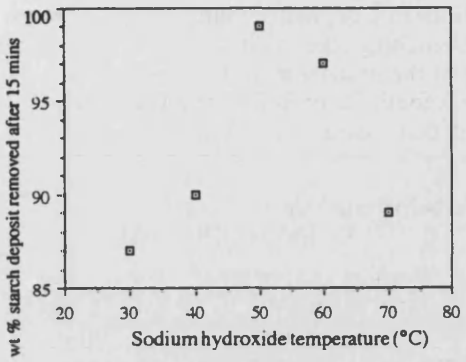


*Figure 5.* Effect of temperature upon the removal of starch deposit cleaned with 14 wt% NaOH.

is seen at 14 wt% when starch is cleaned using nitric acid. To remove 95 wt% of the starch mass took 15 minutes when 14 wt% nitric acid was used, compared to 55 minutes when 20 wt% nitric acid was employed.

*Starch deposit cleaning visualisation*

The deposits were viewed from above during the cleaning process. Visual observation of the behaviour of the starch deposit during cleaning provides clues to the mechanisms involved in the process. When cleaning was carried out with distilled water, deposit swelling was minimal, and the material that was removed came away in small fibres. However, when sodium hydroxide was used swelling was much more marked. At a low sodium hydroxide concentration (1 wt%), stresses set up in the deposit due to swelling removed the central mass of deposit from the stainless plate very slowly. Any remaining deposit was subsequently dissolved into the cleaning solution. At a higher concentration of sodium hydroxide (10 wt%), swelling was very rapid, and soil/substrate bonds were broken whilst soil/soil bonds remained intact. This resulted in the removal of large amounts of starch deposit in an aggregated mass. The action of sodium hydroxide in removal can be contrasted to that of nitric acid, which facilitated removal of starch aggregates of 0.1–1.0 mm in diameter from the bulk of the deposit mass. Protein deposits swell on contact with sodium hydroxide; it is possible that protein removal models such as those described in Bird and Fryer[8] and

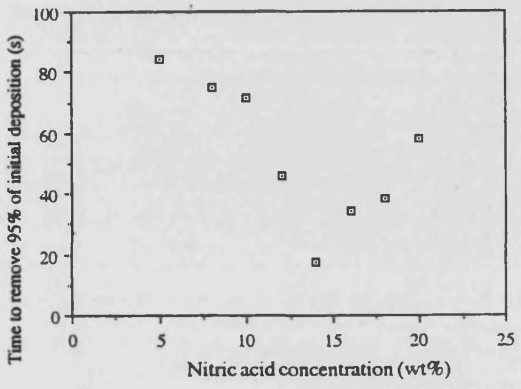


*Figure 6.* Effect of concentration upon the removal of starch deposit cleaned with nitric acid at 50°C.

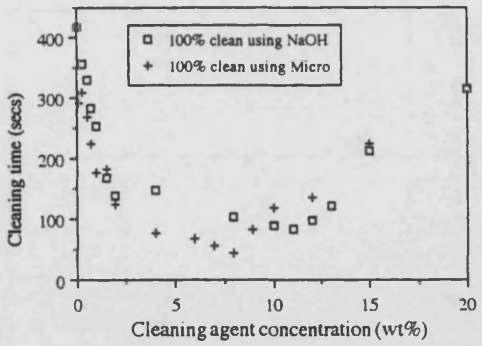


*Figure 7.* Effect of sodium hydroxide and *Micro* concentration upon glucose deposit removal at 30°C.

Bird[9], may well be appropriate in modelling starch removal processes.

*Glucose deposit cleaning experiments*

Glucose deposits were cleaned using a range of chemical cleaning agents, and the cleaning time recorded when the sample plate was visually clean. The most effective of the cleaning agents tested were found to be sodium hydroxide and *Micro* commercial cleaner (International Products Corporation). *Micro* is a multi purpose cleaning agent primarily consisting of anionic surfactants supplemented with quaternary ammonium compounds and ethoxylates. A detailed sodium hydroxide concentration sweep was carried out for concentrations 0.25–20 wt% (Figure 7). A definite optimum concentration exists for cleaning in the shortest time, occurring at 11 wt% sodium hydroxide. The range of concentrations which give an acceptable performance is 4–12 wt%. The use of a concentration of 20 wt% results in the same cleaning performance as when 1 wt% sodium hydroxide is used.

Cleaning with *Micro* at 30°C using concentrations of 0.1–15 wt% showed that an optimum concentration exists at 8 wt% (Figure 7). Cleaning agent concentrations in the range 4–9 wt% cleaned the sample plates in the shortest time. The use of 15 wt% *Micro* results in the same cleaning time as the use of 1 wt%.

*Glucose cleaning conclusions*

The cleaning time was a strong function of the cleaning agent concentration, and a cleaning time minimum was found for both *Micro* and sodium hydroxide solutions. Higher or lower cleaning agent concentrations resulted in longer total cleaning times. No optimum temperature was observed when removing glucose deposits, in contrast to the starch deposit removal temperature optimum.

In addition to detailed experimental verification of fouling and cleaning reproducibility, further study of carbohydrate cleaning must link experimental observations to mechanistic considerations. If mechanisms are found to be universal rather than an artefact of the system studied, then predicting and optimising cleaning processes will be simpler.

## CLEANING MICROFILTRATION MEMBRANES FOULED WITH WHEY PROTEINS

The operation of pressure driven membrane systems

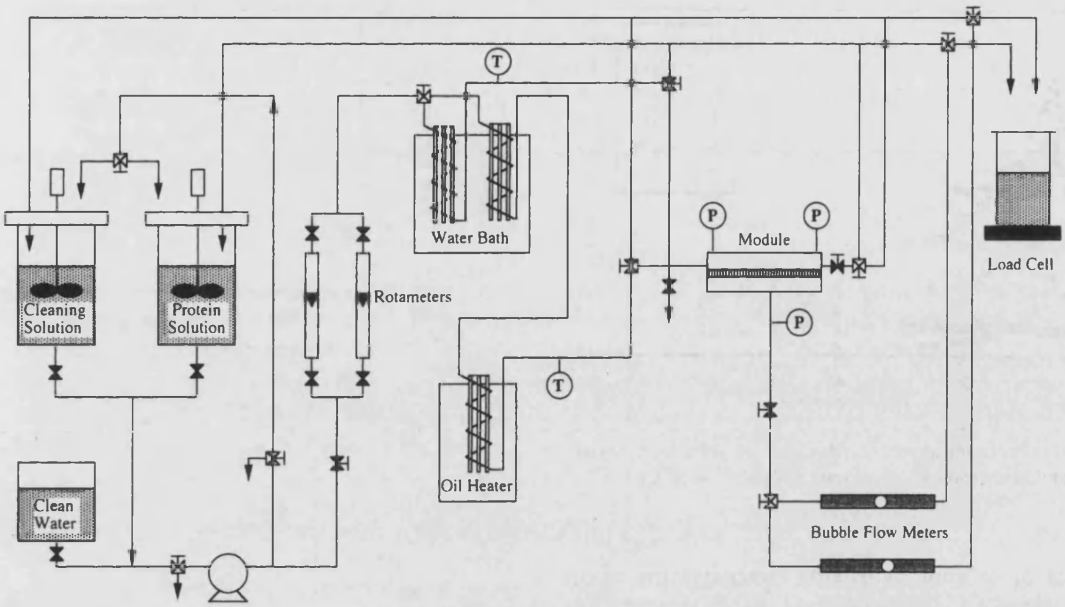


*Figure 8.* Schematic diagram of the membrane fouling and cleaning apparatus.

is inevitably limited by fouling phenomena, causing a decline in permeation rate. Although in certain circumstances it is possible to delay the onset and/or reduce the amount of fouling, it is unlikely that fouling will be completely eliminated[14,15,16,17]. Therefore membrane cleaning is essential to ensure hygienic opera-tion and maintain the permeate rate and quality.

The removal of whey protein deposits from stainless steel surfaces has been evaluated[7,9] and the transfer of knowledge from hard surfaces to membrane systems is the novel approach central to this investigation. An experimental protocol has been devised in which the hard surface/membrane system cleaning similarity is high and moves away to encompass wider systems.

An experimental apparatus has been designed and constructed to generate fouled membrane samples and then clean them *in situ* under controlled thermo-hydraulic conditions. A combined fouling and cleaning rig (Figure 8) utilises a stainless steel module designed to house any flat-sheet membrane of size 100 mm × 100 mm[18]. This paper reviews the results from cleaning sintered stainless steel microfiltration membranes of 2 $\mu$m nominal pore size (Pall Filtration Ltd).

## Membrane Fouling

To determine the effectiveness of each cleaning procedure, a reproducible deposit must be generated. Used and restored membranes were conditioned by circulating a 50 mM solution of sodium nitrate (Sigma Laboratories Ltd) at 50°C with a trans-membrane pressure (TMP) of 0.5 bar and a cross flow velocity (CFV) of 1.6 $ms^{-1}$ for 1 hour. Immediately after conditioning, the membrane sections were fouled using a solution of a reconstituted whey protein concentrate powder (WPC) (Carbelac 35, Carbery Milk Products) for 1 hour. A 3.5 wt% protein solution (pH 6.4) was employed throughout the study using a CFV of 1.0 $ms^{-1}$ and a TMP of 1.0 bar during the microfiltration run of 1 hour. Retentate and permeate were recirculated back to the feed tank. Permeate flux during the microfiltration operation was monitored to check the progression of the fouling process (Figure 9), and to ensure that a reproducible and sufficiently severe deposit was generated[19].

## Membrane Cleaning Results

Typical flux recovery curves obtained during cleaning are presented in Figure 10, and show that initially low flux values quickly increase to a maximum before decaying to a terminal flux. Whilst the ultimate flux recovery value at the end of the cleaning procedures is important, the shape of the flux recovery curves themselves can be characterised in terms of a maximum flux recovery, the time to reach the maximum and the rate of decline from the maximum. This information is necessary if membrane cleaning operations are to be optimised in terms of time and cost.

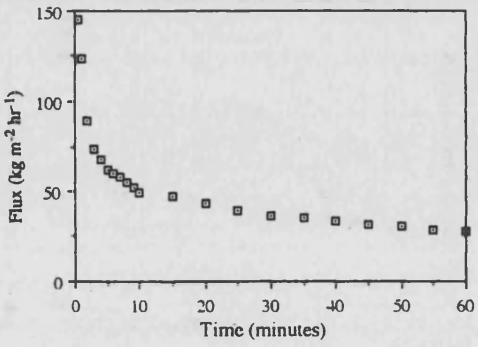


*Figure 9.* Flux decline curve during fouling. For an MF membrane fouled with 3.5 wt% WPC solution at 50°C, TMP of 1.0 bar, and CFV at 1.0 $ms^{-1}$.

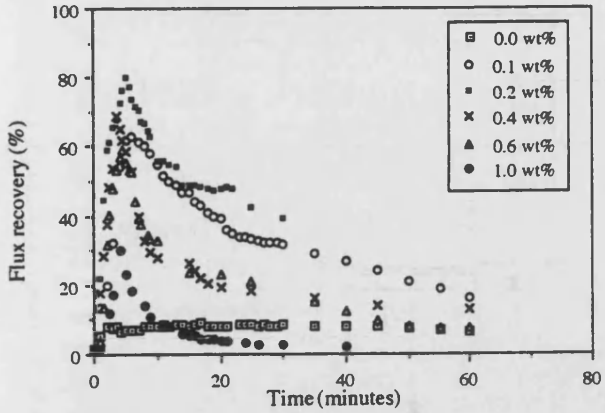


*Figure 10.* Effect of concentration upon flux recovery for a whey protein fouled MF membrane cleaned with sodium hydroxide at 50°C, TMP of 0.5 bar, CFV of 1.6 $ms^{-1}$.

The effect of sodium hydroxide concentration upon membrane cleaning was examined at a temperature of 50°C and CFV of 1.6 $ms^{-1}$. A TMP of 0.5 bar was employed so that the flux recovery during the cleaning process could be monitored. Figure 10 shows the effect of concentration on the maximum flux recovery values obtained represented as a percentage of the water flux value for the clean and restored membrane[19].

Using water to clean the fouled membrane results in only a small flux recovery, amounting to no more than 8% of the possible membrane flux. As the sodium hydroxide concentration is increased, so the flux recovery increases dramatically. The use of 0.2 wt% results in an optimal maximum flux recovery of 80%. Further increases in sodium hydroxide concentration do not aid the flux recovery process but result in lower maximum flux recovery values. The use of 1 wt% results in approximately the same maximum flux recovery as when 0.05 wt% is used.

The time taken to reach the maximum flux recovery shows an initial steep decline from 25 minutes when water is used to clean the membrane, to 6 minutes when 0.1 wt% sodium hydroxide is employed. The effect in changing concentration from 0.1–0.75 wt% upon the time to reach the point of maximum flux recovery is a steady drop from 6 minutes to 1 minute.

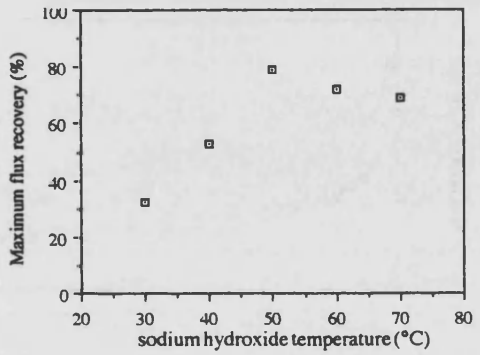


*Figure 11.* Effect of temperature upon removal for a WPC fouled membrane cleaned using 0.2 wt% NaOH, CFV of 1.6 $ms^{-1}$, TMP of 0.5 bar.

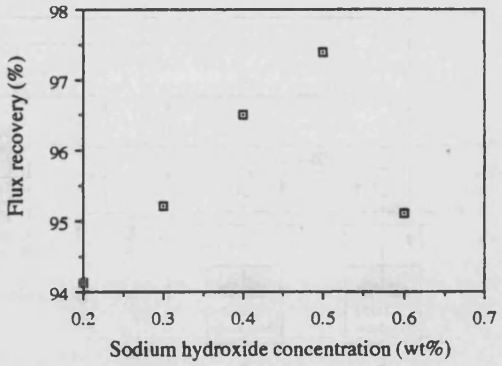


*Figure 12.* Effect of concentration upon WPC removal cleaned with NaOH at 50°C, CFV of 1.6 $ms^{-1}$, zero TMP.

The effect of cleaning solution temperature upon the maximum flux recovery is shown in Figure 11. Temperatures in the range 30–70°C were investigated using a sodium hydroxide concentration of 0.2 wt%, a TMP of 0.5 bar and a CFV 1.6 $ms^{-1}$. An optimum temperature of 50°C is found, giving a maximum flux recovery value of 80%. Further increases in temperature result in decreases in the maximum flux value, and a temperature of 70°C results in a maximum flux recovery of only 69%. The time to reach the maximum decreases with increasing temperature from 8 minutes at 40°C to 30 seconds at 70°C.

The difference in flux recovery between operation in either laminar or turbulent flow conditions was not marked. Reynolds numbers of 1500–6000 were investigated, and only a very small increase in flux recovery was recorded[20]. In this system, cleaning procedures utilising laminar flow conditions are therefore likely to be more economical.

The absence of an applied pressure during cleaning produced the highest flux recovery. A 30 minute clean with 0.2 wt% sodium hydroxide resulted in a >94% flux recovery. The use of a TMP greater or equal to the conditions used during fouling gave a reduced cleaning performance. It appears that the application of even a low TMP may cause some compaction of the deposit during cleaning.

As a result of these observations, further experiments were carried out to demonstrate the effect of sodium hydroxide concentration on flux recovery using zero TMP (Figure 12). This results in a sustainable flux recovery >97% when using a sodium hydroxide concentration of 0.5 wt% after a 30 minute cleaning period. This concentration optimum agrees with the value found for proteinaceous deposit removal from hard surfaces[7,9].

## Membrane Cleaning Mechanisms

Concentration optima found when cleaning protein based deposits from hard surfaces were explained in terms of the morphological changes the deposit underwent on contact with sodium hydroxide; the maximum deposit voidage occurring at the optimum concentration[9]. Work is currently under way to examine changes in the nature of the deposit on the membrane surface as a function of sodium hydroxide concentration;

the swelling of both loosely bound and pore blocking material is clearly concentration dependent, and might also be explained in terms of morphological changes as well as deposit interactions with the porous membrane structure. The optimum sodium hydroxide concentration value for membrane cleaning using a positive TMP, 0.2 wt%, differs greatly to that found at zero TMP and for hard surface protein removal, of 0.5 wt%. This is not surprising when considering the differences in surface material structure.

An optimum temperature of 50°C found for cleaning microfiltration membranes may be explained in terms of the structure of the swollen deposit. At low temperatures any increase will aid the cleaning process by speeding up the chemistry of deposit breakdown and dissolution, while decreasing the cleaning solution viscosity and hence increasing the Reynolds number. However, high temperatures have been found to produce a tenacious deposit with a high swelling capacity which is not susceptible to breakdown by sodium hydroxide[9,19]. The inverse solubility with temperature displayed by calcium phosphate deposited from the WPC solution[21] may also slow cleaning at high temperatures.

As cleaning progresses beyond the point where the maximum flux recovery value occurs the highly swollen deposit may be forced into the membrane pores, leading to flux decline to a terminal value. This phenomena has also been reported by Parkin and Marshall[22] for the removal of whey proteins from cellulose acetate ultrafiltration membranes. The authors suggested that for optimum cleaning performance, cleaning should not progress beyond the point of the maximum flux recovery.

A schematic presentation of the proposed removal mechanisms is shown in Figure 13(a)–(h).

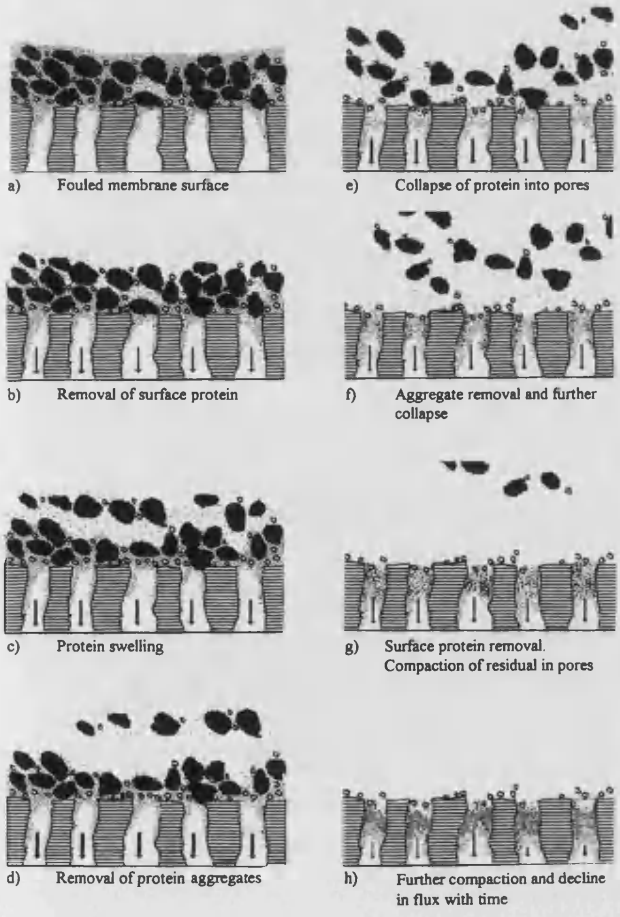


*Figure 13.* Schematic diagram of removal mechanisms.

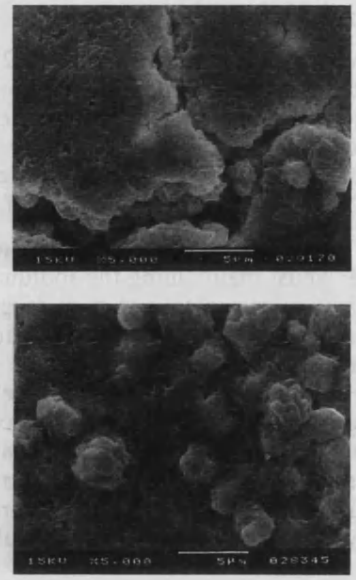

*Figure 14a.* Species 1 material is loosely bound to the membrane surface.
*Figure 14b.* Species 2 material is more tightly bound and may be present in the pores of the membrane.

## A Membrane Cleaning Model

The characteristic curve shapes shown in Figure 10 can be explained in terms of the existence of two deposit species. Species 1 is loosely bound material attached to the membrane surface (Figure 14(a)), while Species 2 (Figure 14(b)) is more tightly bound and may be present in the pores of the membrane. Species 1 may be fractured and removed relatively easily by a combination of chemical interaction and fluid mechanical shear. Species 2 which is more tightly bound to the membrane than Species 1 and is less likely to be affected greatly by surface shear stresses. Species 2 may swell on contact with sodium hydroxide. It is hypothesised that the deposit may become more susceptible to compaction due to an applied transmembrane force, consequently this leads to a decline from the maximum flux recovery value as the material is forced further into the membrane pores. The decline in flux during cleaning may be further accentuated to the presence of partially hydrolysed protein at the surface and in the pores of the membrane when cleaning using relatively low cross flow velocities.

## Membrane Cleaning Conclusions

Concentration and temperature optima have been shown to exist for the removal of whey proteins from sintered stainless steel microfiltration membranes when cleaned with sodium hydroxide.

These optima occur at:

(i) a sodium hydroxide concentration of 0.2 wt% when cleaning with an applied TMP of 0.5 bar and 0.5 wt% when cleaning with zero TMP (temperature of 50°C and CFV of 1.6 $ms^{-1}$).
(ii) at a temperature of 50°C when utilising a concentration of 0.2 wt% (TMP of 0.5 bar, CFV of 1.6 $ms^{-1}$).

From the proposed qualitative model, altering the CFV or TMP whilst maintaining the sodium hydroxide concentration should lead to a shift in magnitude and time of the maximum flux recovery. Changing the concentration should primarily affect the value of the final flux recovery and the rate of decline from the maximum, whilst having a smaller effect upon the maximum flux recovery. Changes in the chemical composition of the cleaning agent, such as the addition of surfactants to the sodium hydroxide, should lead to a more sustained flux recovery. Observed experimental results support these trends.

Removal mechanisms have been proposed to describe the experimental flux values observed during cleaning and a qualitative model has been developed which enables a partial separation of the chemical and fluid dynamic effects in the cleaning process to be made.

## CONCENTRATION AND TEMPERATURE OPTIMA CONCLUSIONS

Cleaning food based deposits involves complex interplay between fluid mechanics and surface chemistry. Concentration and temperature optima occur widely during the removal of protein, starch and glucose based deposit using chemical cleaners. Optimal behaviour can be linked in many cases to changes in the deposit morphology as a function of concentration and temperature. An understanding of concentration and temperature optima is necessary if industrial cleaning in general, and CIP in particular, is to be optimised.

## REFERENCES


1. Graßhoff, A., 1989, Environmental aspects of the use of alkaline cleaning solutions, in *Fouling and Cleaning in Food Processing*, Kessler, H. G. and Lund, D. B. (eds.), 107–114 (Munich University, FRG).
2. Romney, A. J. D., 1990, *CIP: Cleaning in Place*,(Society of Dairy Technology).
3. Pritchard, A. M., 1988. The economics of fouling, in *Fouling in Process Plant*, pp 14–31. (London: Inst Corrosion Science).
4. Bird, M. R. and Espig, S. W. P., 1994, Cost optimisation of dairy cleaning in place (CIP) cycles, *Trans IChemE, Part C*, 72: 17–20.
5. Gotham, S. M., 1990, Mechanisms of protein fouling of heat exchangers, *PhD Thesis* (University of Cambridge, UK).
6. Bradford, M., 1976, A rapid and sensitive method for the quantification of microgram quantities of protein utilising the principle of protein-dye binding, *Anal Biochem*, 72: 248–254.
7. Bird, M. R. and Fryer, P. J., 1991, An experimental study of the cleaning of surfaces fouled by whey proteins, *Trans IChemE, Part C*, 69: 13–21.
8. Bird, M. R. and Fryer, P. J., 1992, An analytical model for the cleaning of food process plant, *IChemE Symp Series No. 126*, 325–330.
9. Bird, M. R., 1993, Cleaning of food process plant, *PhD Thesis*, (University of Cambridge, UK).
10. Fryer, P. J. and Bird, M. R., 1994, Factors which affect the kinetics of cleaning dairy soils, *Food Sci and Technol Today*, 8: 1, 36–42.
11. Cheow, C. S. and Jackson, A. T., 1982, Circulation cleaning of a plate heat exchanger fouled by tomato juice (i) Cleaning with water and (ii) Cleaning with caustic soda solution, *J Food Technol*, 17: 417–440.
12. Maruyama, Y., Shibata, Y. and Watanabe, K., 1991, A proposed design method for predicting cleaning parameters of the bio-plant, *World Congress of Chem Eng 1991*, session 7.5-4.
13. Bird, M. R., Milford, B. G. and Tucker, B. J., 1994, The removal of carbohydrate based deposits from stainless steel surfaces using chemical cleaning agents, *IChemE Research Event*, pp 529–531.
14. Chen, V., Fane, A. G. and Fell, J., 1992, The use of anionic surfactants for reducing fouling in ultrafiltration membranes: Their effects and optimisation, *J Mem Sci*, 67: 249–261.
15. Mackley, M. R. and Sherman, N. E., 1993, Cake filtration mechanisms in steady and unsteady flows, *J Mem Sci*, 77: 113–121.
16. Robinson, C. W., Siegel, M. H., Condemine, A., Fee, C., Faridy, T. Z. and Glick, B. R., 1993, Pulsed-electric-field cross flow ultrafiltration of BSA, *J Mem Sci*, 80: 209–220.
17. Gan, Q., Howell, J. A., Bird, M. R., England, R. and Field, R. W., 1994, Fouling and backflushing in beer clarification using ceramic membranes, *Food Process Engineering, 4th Bath Food Engineering Conf, Bath, Avon, 19–21 September 1994.*
18. Bartlett, M., Bird, M. R. and Howell, J. A., 1994, Chemical cleaning of fouled membrane systems, *IChemE Research Event*, pp 449–452.
19. Bartlett, M., Bird, M. R. and Howell, J. A., 1994, Effective cleaning of microfiltration membranes fouled during whey protein processing, *Food Process Engineering, 4th Bath Food Engineering Conf, Bath, Avon, 19–21 September 1994.*
20. Bartlett, M., Bird, M. R. and Howell, J. A., 1995, A qualitative model for cleaning whey protein fouled microfiltration membranes, in press, *J Membrane Sci.*
21. Green, M. L., Foster, C. L. and Bitten, M., 1988, Formation and adhesion of deposit to heated surfaces in contact with milk, in *Fouling in Process Plant*, pp 183–196, (Institute of Corrosion Science and Technology, London).
22. Parkin, M. F. and Marshall, K. R., 1976, The cleaning of tubular cellulose acetate ultrafiltration membranes, *N Zealand J Dairy Sci and Tech*, 11: 107–113.
23. Bowen, W. R. and Sabundi, H. A. M., 1992, Pulsed electrophoretic membrane cleaning *IChemE Research Event*, pp 92–94.


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